Development of an Industrial Effluent Treatment Catalyst from Low Value Fleeces

By

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Abstract

This work is devoted to adding value to low value wool by the development of a solid phase oxidation catalyst supported on wool for the treatment of industrial wastewater. It is recognised that homogeneous systems have distinct disadvantages. They introduce metal cation pollutants into sewage, are not easy to replace, cannot be regenerated or used catalytically. As yet very few attempts have been made to develop a heterogeneous oxidation catalyst based on the hydrogen peroxide / Iron (III) system, and no attempts have been made using wool fibre as support. The few solid phase catalysts reported in the literature act by leaching iron (II) or (III) from the catalyst, whereupon catalysis takes place in the homogeneous phase. Immobilisation of a metal cation on wool fibre whilst still remaining catalytically active towards the decomposition of organic molecules in the absence of UV light is not trivial. It is crucially dependant on the nature of the immobilisation.

Raw wool and scoured wools were investigated in their use as a wool catalyst. Modification regimes involving hydroxylamine and hydrazine combinations were evaluated. Both modified and unmodified wool samples were then impregnated with iron. Wool fibres were characterised physically and chemically for the various treatment regimes using a range of techniques including, Fibre Diameter Analysis, Tensile Strength, Scanning Electron Microscope, Energy Dispersive X-ray and Infra-red Spectroscopy.

All wools treated were investigated for their catalytic activity against phenol. Static batch and dynamic studies were carried out to determine reproducibility between samples and catalyst lifetime. It was found that the Iron (III) wool catalyst in the presence of hydrogen peroxide and air was able to oxidise phenol rapidly. Catalytic activity and lifetime of the catalysts were improved with the use of an impregnation mixture of Iron with Calcium or Lithium Salts.

Chromatographic techniques were used to determine the products formed throughout catalysis and confirm that phenol was oxidised according to the routes discussed in literature. Total Organic Carbon (TOC) studies were also conducted to investigate the reduction that could be achieved with the use of the wool catalyst.

Finally, two effluents were provided containing phenolics in varying amounts and concentration by Chemtura and A H Marks. Static and dynamic evaluations were carried out to determine catalyst performance and longevity. Results were positive and showed potential in this area of effluent treatment. This was further supported by the wool catalyst's ability to reduce TOC for both effluents.

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Chapter 1 Literature Review

1.1 Physical Structure of Wool

Wool is a member of the keratin protein group. Other members of this group include hair, feathers, beaks, claws, hooves, horn and even certain types of skin tumour. Wool is produced in the fibre follicle in the skin of sheep. Cells within the fibre begin growing at the follicle base, which is bulbous in shape, and complete their growth above the bulb. This is where keratinisation occurs. The process is completed before the fibre emerges above the skin surface and involves oxidation of thiols to form disulphide bonds. It is disulphide bonds which stabilise the fibre structure (HARDING and ROGERS, 1999).

Wool fibres show a great variation in both physical and chemical properties. This is due to the multitude of variations possible in diet, breed, health and climate etc. Physical properties which are expected to vary include fibre diameter, length and crimp. The chemical constitution of the fibres can also vary. Properties of wool fibre can vary from tip to root (HARDING and ROGERS, 1999). The main differences between high and low value fleeces are physical. Wool is graded by breaking up of the fleece based on overall quality. Higher quality wool comes from the shoulders and sides of the sheep, whereas lower quality comes from the lower legs. Better quality wool is used in clothing and lower quality for making rugs. High quality does not always mean high durability. Major physical characteristics of wool include fibre diameter (fineness or grade), staple length, and clean wool yield. Grade refers specifically to mean fibre diameter and its variability. Fibre diameter is the most important manufacturing characteristic. Wool is classified as follows;

1. Fine – short-staple wool (Merino fineness) 2 inches or more in length.
2. Medium – or mutton 2.5 to 6 inches long.
3. Long-Staple – loosely crimped fibres 10 to 15 inches long.
4. Carpet – long, strong, coarse and blended fibres 1 to 15 inches long.

The wools that are to be investigated fall into the later categories, if any.

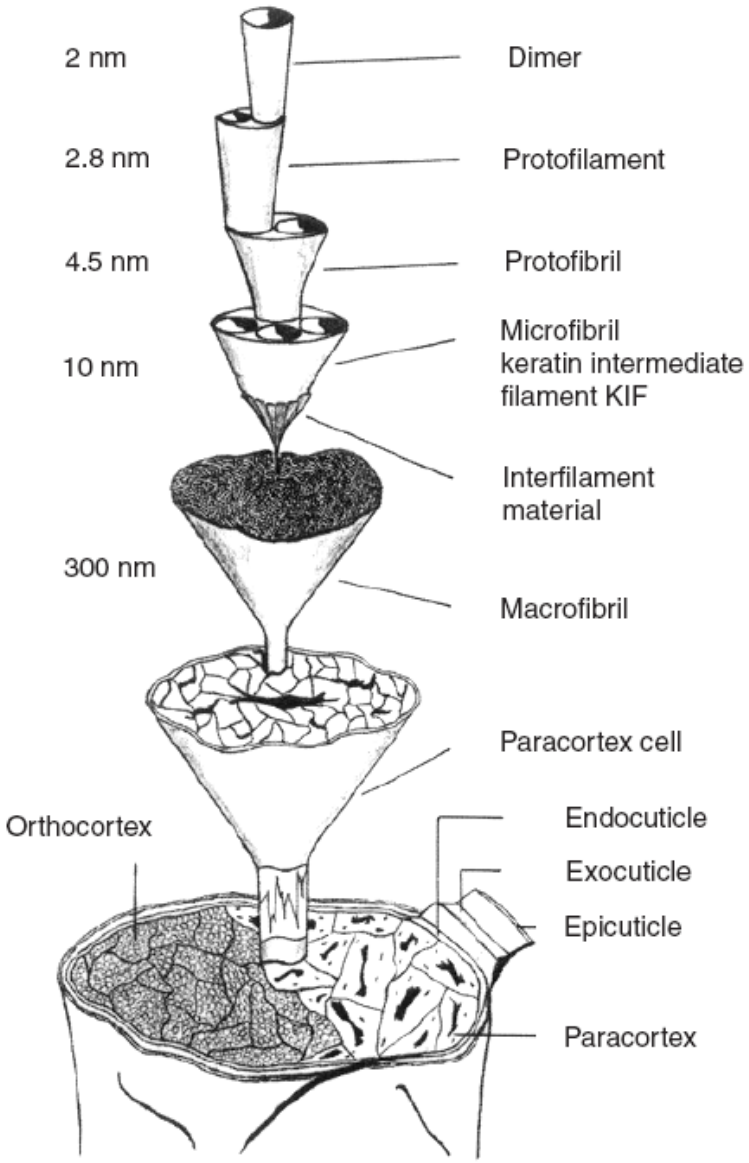


Figure 1.1 Physical structure of wool (SIMPSON and CRAWSHAW, 2002)

There are two types of cell that make up the fibre composition. These are the cuticle cells and the cortical cells. The cuticle cells comprise 10% of the fibre mass and surround the fibre. They overlap in one direction and consist of four layers, the hydrophobic epicuticle, the A- and B-layers of the enzyme-resistant exocuticle and the enzyme-digestible endocuticle (SIMPSON and CRAWSHAW, 2002). Figure 1.1 displays a schematic diagram of the physical structure of wool fibre. The cuticle cells are separated from underlying cortical cells by intercellular cement, which acts like a 'glue'. This is also known as the cell membrane complex comprising of internal lipids

and proteins. It guarantees strong intercellular bonding via proteins generally called desmosomes (SIMPSON and CRAWSHAW, 2002). The epicuticle of wool is strongly hydrophobic and forms a resistant barrier to dyes. However, it can be readily damaged by weathering, mechanical or chemical processes. Chemical treatments such as chlorination cause extensive damage to the epicuticle. The remaining 90% of wool fibre is made up of cortical cells which comprise the cortex of the fibre. This has a bilateral structure and can be subdivided into two parts, orthocortex (60-90%) and paracortex (10-40%) (SIMPSON and CRAWSHAW, 2002). The orthocortex has a more open structure (SHAO, 1998) and is more chemically reactive than the paracortex. It is known that the paracortex has greater sulphur content than the orthocortex. This makes it tougher and more highly cross-linked (SIMPSON and CRAWSHAW, 2002).

1.2 Chemistry of Wool

1.2.1 Chemical composition

The chemical composition and structure of wool is very complex. All types of wool contain carbon, hydrogen, oxygen, nitrogen and sulphur. The amounts present are approximately the same for all species. Table 1.1 provides the elemental composition of untreated wool (BELL, 1955).

Table 1.1 Elemental composition of untreated wool

Element	% by Weight
Carbon	49.2
Hydrogen	6.6
Oxygen	24.7
Nitrogen	15.8
Sulphur	3.7
Ash Content	0.5-1.0

Side chains of wool polypeptides (R) are classified as inert and un-reactive. They also have either acidic or basic terminating groups. The typical amino acid composition is given in Table 1.2 (SIMPSON and CRAWSHAW, 2002) (Appendix 1). Cystine plays

an important role within the wool molecule enabling two polypeptide chains to be linked together by a disulphide bond which is a very strong covalent bond.

Table 1.2 Typical amino acid (AA) composition of wool

Amino Acid (AA)	AA Abbreviation	Concentration (μmol/g)
INERT		
Alanine	Ala	470
Glycine	Gly	760
Isoleucine	Ile	270
Leucine	Leu	680
Phenylalanine	Phe	260
Proline	Pro	520
Valine	Val	490
ACIDIC (and their ω-amides)		
Asparagine	As	360
Aspartic Acid	Asp	200
Glutamine	Gl	450
Glutamic Acid	Glu	600
BASIC		
Arginine	Arg	600
Histidine	His	80
Lysine	Lys	250
HYDROXYL		
Serine	Ser	900
Threonine	Thre	570
Tyrosine	Tyr	350
SULPHUR-CONTAINING		
Cysteine	Cys	10
Cysteic acid		10
Cystine		460
Thiocysteine		5
Lanthionine	Lan	5
Methionine	Met	50
MISCELLANEOUS		
Tryptophan	Tryp	40

Figure 1.2 provides a schematic illustration of a wool molecule. Not all of the amino acids are shown and it may not be a true indication of the arrangement. There are believed to be approximately 500 amino acid residues present in wool. This can vary between different species as well as the quantities.

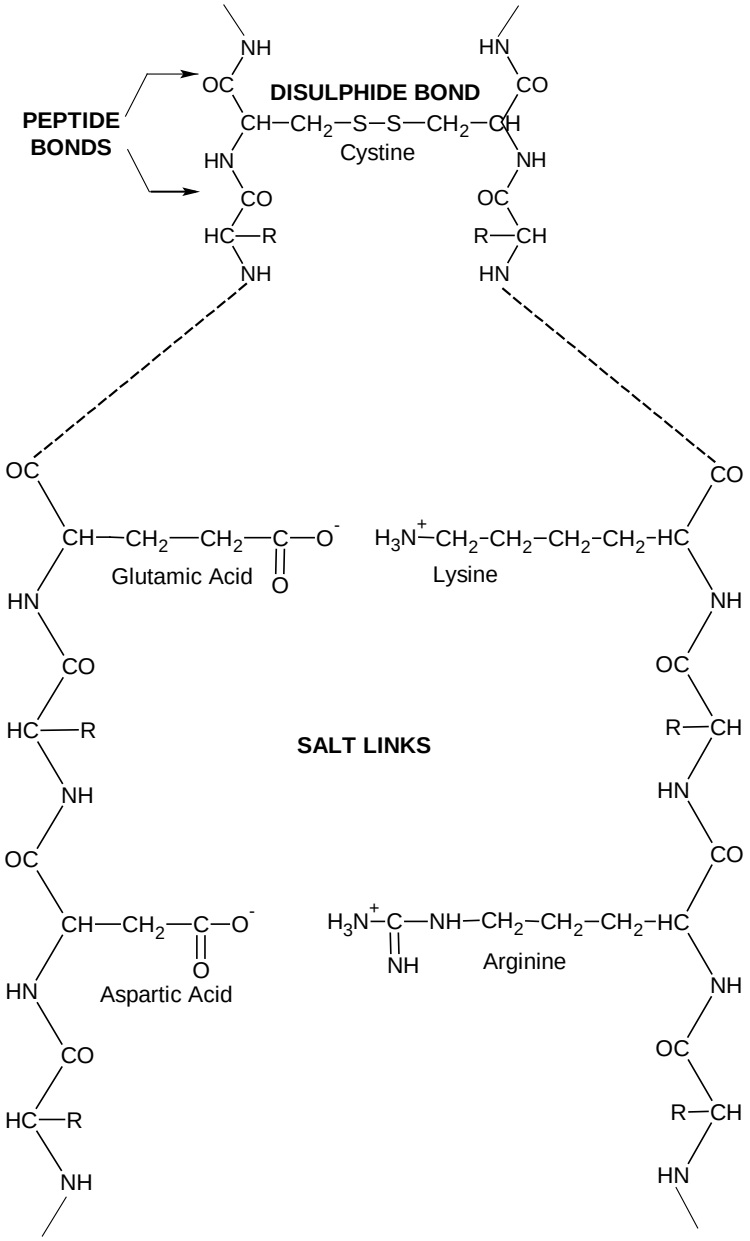


Figure 1.2 Schematic illustration of a wool molecule (BELL, 1955)

Three types of bonding exist in wool. The disulphide bond as already mentioned, the salt-link as shown in the schematic and finally hydrogen bonding. Salt-linkages are also referred to as electrostatic or acid-base bonds. The strength of such bonds is reduced

when wool is placed in a highly dielectric medium, for example water. Hydrogen bonding is greatest in the crystalline regions of the fibre i.e. wherein chains are well oriented (BELL, 1955). This is illustrated in Figure 1.3. In amorphous zones chains are not close enough to facilitate hydrogen bonding.

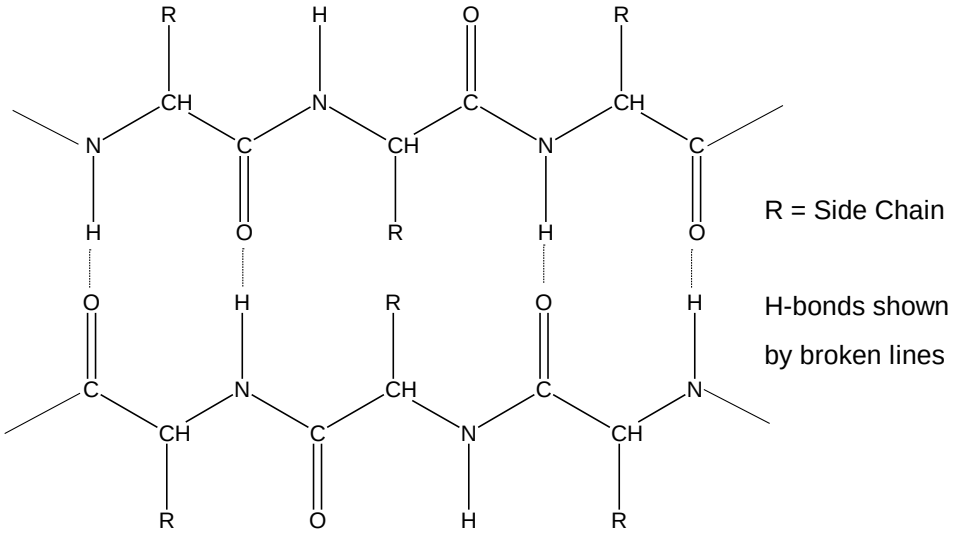


Figure 1.3 Hydrogen bonding in wool

The greatest numbers of stabilising interactions are delivered by the hydrogen bonding. These occur at the following (ZAHN and KNOTT, 1992):

a) Between peptide bonds within the helices,
b) Between peptide bonds within non-helical chain sections,
c) Between peptide bonds of adjacent cells,
d) Between peptide bonds and side chain groups,
e) Between side chain groups (e.g. asparagines and glutamine, serine, threonine, histidine, tyrosine).

1.2.2 Chemical reactions of wool

Wool is not a chemically resistant fibre. All bonds are open to attack by acids and alkalis, as well as by oxidising and reducing agents (BELL, 1955). This section gives detailed examples of reactions involving wool.

Reactions of wool to dry heat

Prolonged treatment at 120^{o}C causes a decrease in solubility (as tested by urea/bisulphite solutions). After further heating, 140-179^{o}C, yellowing or brown colouration occurs where alkali solubility increases and urea/bisulphite solubility decreases, indicating alkali damage to the wool (i.e. decomposition of amide groups). The breaking strength, elastic modulus and equilibrium regain of wool become decreased. Changes in the fibre surface include contraction, wrinkling and bubble formation. Changes also occur in the surface area and porosity. Above 200^{o}C cystine residues decompose and heating at 220-250^{o}C (under vacuum) causes the helical regions of the fibre to melt. This is known as the "melting-point" which can be influenced by the rate of heating (ZAHN and KNOTT, 1992).

When wool is heated it absorbs oxygen and a variety of reactions occur. Amino, amide and disulphide groups can be destroyed. The destruction of cystine residues is accompanied by the formation of lanthionine, lanthionine sulphoxide, lysinoalanine, β-aminoalanine, and cysteic acid residues.

Chemical changes in wool due to heat and water

When heated in water progressive decomposition of wool proteins occur. The dissolution of degraded proteins depends on the pH of solution, temperature and reaction time. The helical crystalline region becomes destroyed at temperatures above 130^{o}C. Isoionic wool, produced at pH 4.9 contains an equal number of positive and negative charges, and is more stable towards hydrolysis than wool containing residual acids or alkalis (ZAHN and KNOTT, 1992). Alkali containing wool produces aqueous extracts at pH 7-10 due to residual alkalis content and is degraded in water readily at

temperatures as low as 55°C. Important chemical reactions under alkaline conditions are given below in Figure 1.4 and Figure 1.5.

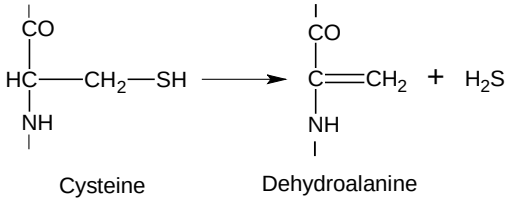


Figure 1.4 Decomposition of cysteine residues to dehydroalanine and hydrogen sulphide (ZAHN and KNOTT, 1992)

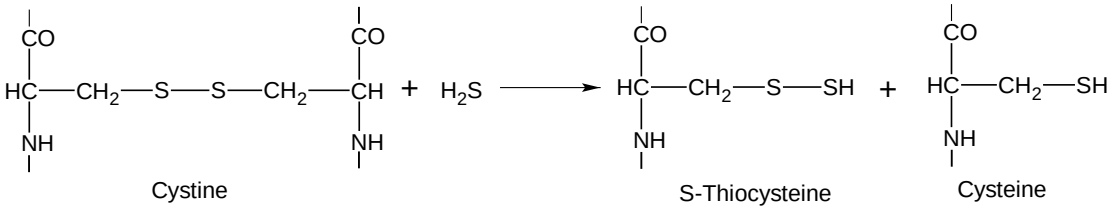


Figure 1.5 Further reaction involving cystine and hydrogen sulphide (ZAHN and KNOTT, 1992)

Lanthionine can be detected in hydrolysates of wool boiled in water at pH 5-7 for one hour. Boiling in solutions at a pH greater than 9 causes an increase in lanthionine formation. This reaction is given in Figure 1.6. A final important reaction involving water is the formation of aspartic acid. This is demonstrated in Figure 1.7.

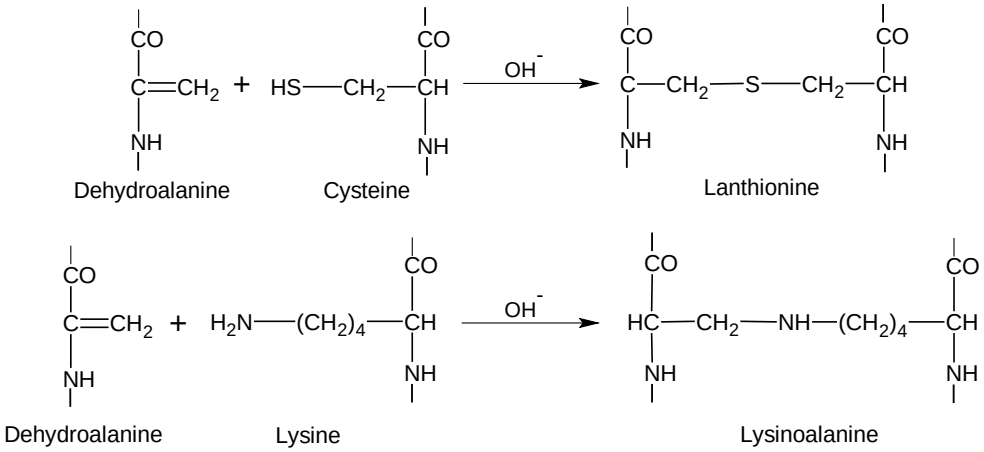


Figure 1.6 Formation of lanthionine and lysinoalanine (ZAHN and KNOTT, 1992)

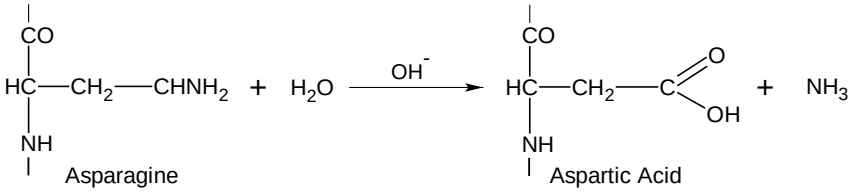


Figure 1.7 Reaction of water and asparagine in the formation if aspartic acid (ZAHN and KNOTT, 1992)

Reactions of wool with acids

An important reaction is the hydrolytic degradation of wool in acids. A typical reaction is given in Figure 1.8. This type of reaction is brought about by hot, concentrated solutions of mineral acids (BELL, 1955). Sulphuric acid reacts readily under cooler temperatures converting wool to a charred residue. This is of great industrial importance.

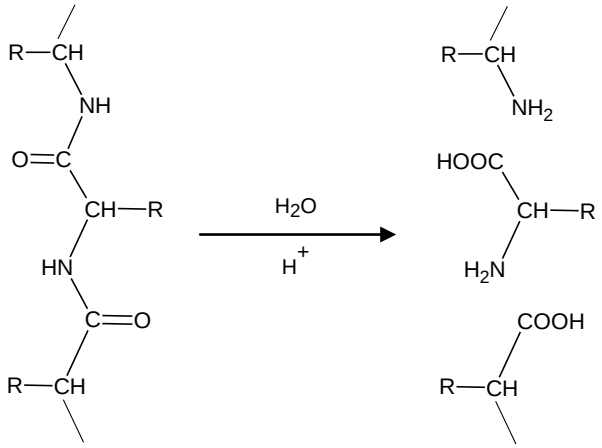


Figure 1.8 Hydrolytic degradation of wool in acids (BELL, 1955)

Carbonising is the treatment of wool with sulphuric acid, followed by drying and baking or dyeing with 1:1 metal complex dyes. Peptide bond hydrolysis can occur during the process leading to weight loss and reduction in tensile strength of wet fibres (ZAHN and KNOTT, 1992). The reaction of peptide bonds with sulphuric acid and water is given below (Figure 1.9). Nitric acid stains the fibre yellow followed by complete

destruction. The colour is due to a side reaction with tyrosine. A more common reagent used in hydrolysis is hydrochloric acid which does not partake in side reactions.

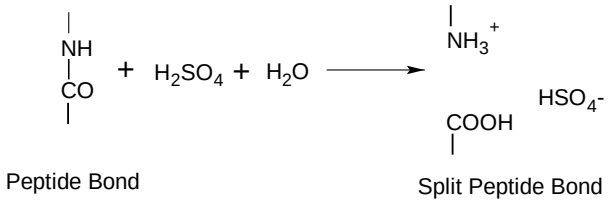


Figure 1.9 Reaction of peptide bond with sulphuric acid in water (ZAHN and KNOTT, 1992)

Another important scheme involves a peptide bond from the main peptide chain being catalysed by sulphuric acid. This is named the N to O-peptidyl shift and is given in Figure 1.10. It is a reversible reaction providing the sulphuric acid is removed at the end of the carbonising process (ZAHN and KNOTT, 1992). If however, carbonized wool containing more than 3% w/w residual sulphuric acid is stored under humid conditions, a slow irreversible hydrolysis takes place. This occurs at the ester bonds in the O-peptidyl structure leading to permanent damage of serine and threonine peptide bonds. Other targets for acid catalysed hydrolysis are asparagine and glutamine.

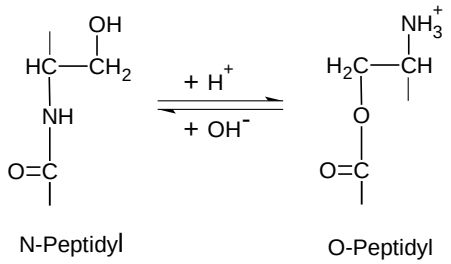


Figure 1.10 N- to O-peptidyl shift (ZAHN and KNOTT, 1992)

Degradation of wool by alkali treatment

There are four main reactions involving the alkali treatment of wool (ZAHN and KNOTT, 1992). These are:

a) Formation of dehydroalanine and hydrogen sulphide from cysteine by β-elimination. (See Figure 1.4 for reaction).
b) Formation of thiocysteine and dehydroalanine from cysteine by β-elimination. (See Figure 1.11 for reaction).
c) Formation of cysteine and sulphur from thiocysteine. (See Figure 1.11 for reaction).
d) Formation of lanthionine by addition of cysteine to dehydroalanine. (See Figure 1.6 for reaction).

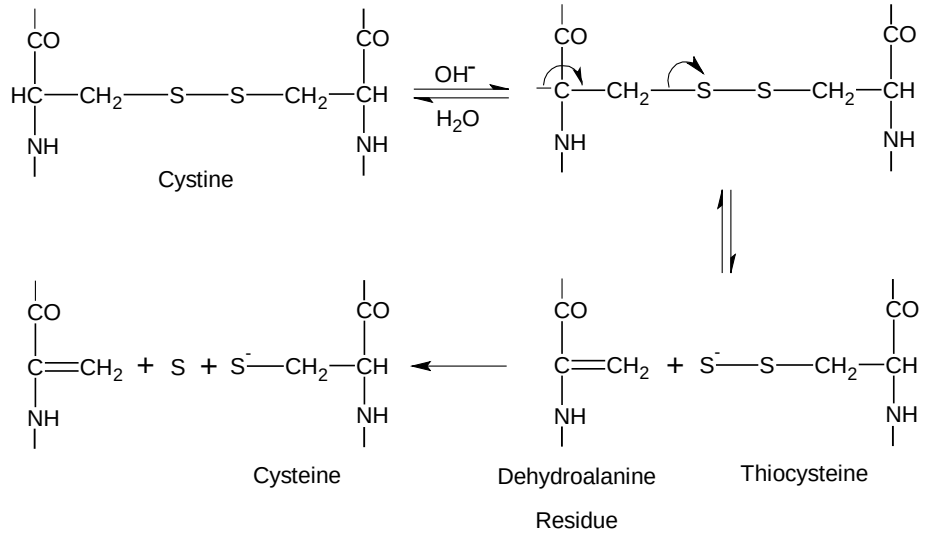


Figure 1.11 Reaction mechanism for the formation of thiocysteine, dehydroalanine, cysteine and thiocysteine (ZAHN and KNOTT, 1992)

This mechanism is supported by the isolation of a pure dehydroalanine containing peptide by alkali treatment. The extent of the reaction of wool with alkali is dependent on the conditions used (temperature, concentration etc.). It has been found that solubility decreases as a result of alkaline treatments under conditions which cause only

small reductions in cystine content. The most sensitive and extensively used method for detecting alkali damage to wool is the urea/bisulphite solubility test.

Reaction of wool with reducing agents

Wool swells rapidly and dissolves in sodium sulphide causing cystine linkages to be reduced to cysteine groups. This is represented in Figure 1.12 below.

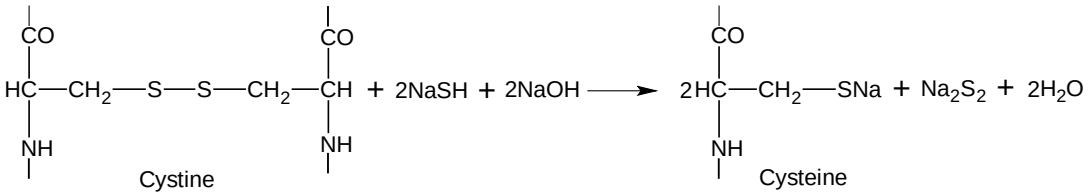


Figure 1.12 Reaction of wool with sodium sulphide (ZAHN and KNOTT, 1992)

Another important application within the wool industry is the reaction with sodium bisulphate (Figure 1.13). This is a partly reversible reaction where cystine can be reformed when wool is washed at pH 5. Wool remains permanently elongated when kept stretched in a dilute bisulphate solution. These reactions are the basis of the permanent pleat setting process of wool.

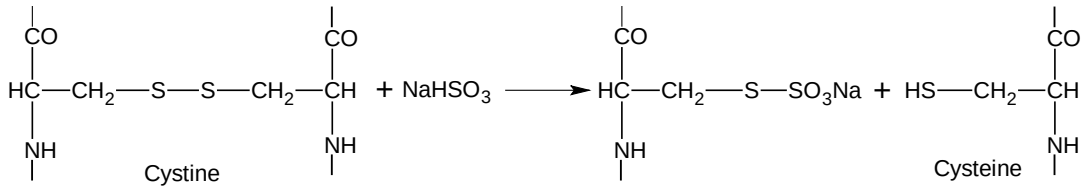


Figure 1.13 Reaction of cystine with sodium bisulphate (ZAHN and KNOTT, 1992)

Wet strength of a fibre post reduction can be lowered to less than one tenth of the original strength. Thiol groups produced by reduction are very labile and can be easily re-oxidised. This can be done by prolonged exposure to the atmosphere or by treatment with mild oxidising agents, e.g. hydrogen peroxide or potassium bromate. As the thiol

groups re-oxidise the wet strength of a fibre can be restored to almost the original value by the formation of disulphide bonds.

Early work by Bradbury (BRADBURY, 1958b and 1958a) investigates the use of anhydrous hydrazine with simple peptides and wool. It was said that treatment for 8 hours at 100-120^{o}C would split peptide bonds to produce amino acid hydrazines and free amino acids from C-terminal positions. The severity of the treatment causes decomposition of cysteine and cystine. However, this can be reduced by the addition of hydrazine sulphate to the reaction mixture. When heating at 60^{o}C for 16 hours this brings about complete fission of the peptide bond (BRADBURY, 1958b). The application of hydrazinolysis with the addition of hydrazine sulphate has been used on wool proteins and wool itself. Work was done by Bradbury (1958a) to study the effect of variation of temperature, water content of the hydrazine and other factors on the yield of C-terminal and non-C-terminal amino acids. However, the results obtained with wool showed the limitations of the method as there were very few, if any, C-terminal groups. McNeil has also used this reducing agent hydrazine sulphate in the study of chemical treatments to wool in order to increase conductivity (McNEIL, 1992). The use of hydrazine sulphate was found to reduce the resistance of copper sulphite treated acrylic fibres. However, when applied to wool, resistances tend to increase. Unfortunately to date, no mechanisms for the reaction of hydrazine with wool have been found in the literature.

The action of oxidising agents on wool

Wool is sensitive to oxidising agents like those used in bleaching. The cystine bonds become oxidised as bleaching agents act upon the disulphide bonds. Methionine, tryptophan, tyrosine and peptide bonds are prone to oxidative degradation reactions. The extent of oxidisation is dependent on the structure of the oxidising agent, its concentration and pH, the reaction temperature and reaction time (ZAHN and KNOTT, 1992). Peroxide bleaching, as well as whitening the wool, results in oxidative attack on the disulphide bonds of cystine (CUDMORE, 1989). When fully oxidised, cystine produces cysteic acid. The overall reaction is summarised in Figure 1.14.

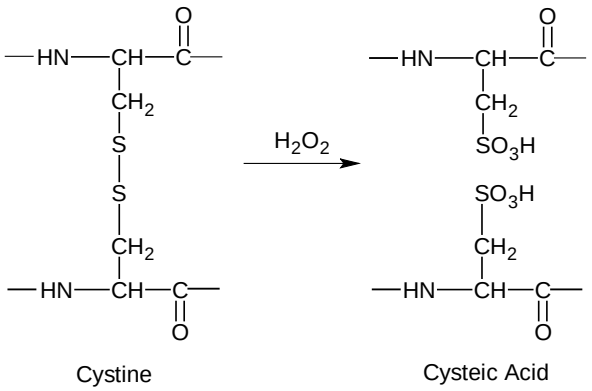


Figure 1.14 Oxidation of cystine to produce cysteic acid (CUDMORE, 1989)

The breaking of the cystine cross-link produces sulphonic acid groups and modifies wool keratin. These modifications can be both chemical and mechanical.

Reaction of wool with halogens

Halogen reactions are used within the wool industry to render wool un-shrinkable. Wool can react with all halogens and the reaction with chlorine is very important forming the basis of the anti-shrink process (Figure 1.15). Chlorination of wool by acidic solutions of sodium hypochlorite is dependent on pH. This controls the incidence of hypochlorite anions, hypochlorous acid and chlorine. Halogens react with cystine, sensitive side chains in wool proteins, and with carbon amide bonds (peptide bonds). During chlorination, chloroamides are formed which act like organic derivatives of hypochlorous acid.

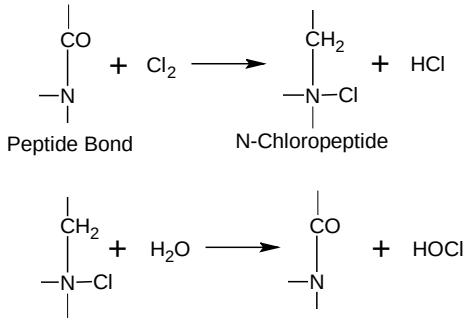


Figure 1.15 Chlorination of wool (ZAHN and KNOTT, 1992)

1.2.3 Dyeing wool

Dyeing with cationic dyes

Wool has a high affinity for basic dyes due to the presence of acid groups. It has been proven that when protein fibres have amine complexes removed the affinity for Methylene blue increases. This is due to the conversion of amide groups into carboxylic residues as a result of exposure to nitrous acid (CEGARRA et al., 1999). This confirms the existence of a salt bond between the fibre and the dye as shown below in Figure 1.16.

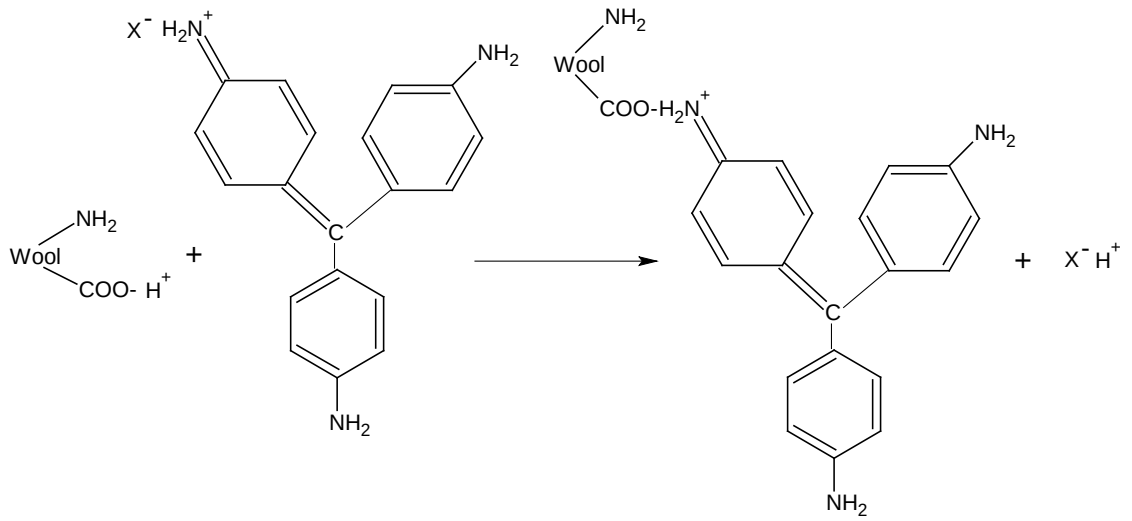
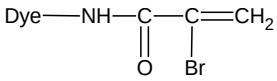
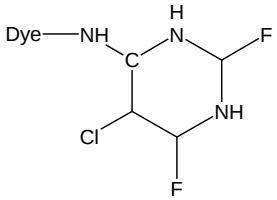
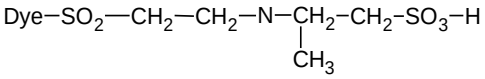


Figure 1.16 The salt-link formation between fibre and dye (CEGARRA et al., 1999)

Dyeing with reactive dyes

Dyes can fix to amine end groups or side chains (cysteine thiolic groups). Reactive dyes differ from any other as they contain functional groups capable of forming covalent bonds with the fibre. A range of reactive dyes applied to wool (CEGARRA et al., 1999) are listed in Table 1.3.

Table 1.3 Reactive dyes applied to wool

Reactive Group	Year of Appearance	Trade Name
Dye-SO_2-CH=CH_2 Dye-SO_2-CH_2-CH_2-OSO_3H Vinylsulphonic and B-Sulphate Ethyl Sulphonic	1952	Remalan (Hoechst)
Dye-NH-CO-CH=CH_2 Acrylamidic Dye-NH-CO-CH_2CI CO-Chloroactylamidic	1964	Procilan (I.C.I)
 α-Bromoacrylamidic	1966	Lanasol (Ciba)
 Difluorichloro Pirimidriyc	1970	Verofix (Bayer) Drimalan (Sandoz) Reacholan (Griegy)
 Methyl Taurine Ethyl Sulphonic	1970	Hostalan (Hoechst)

The union between reactive dyes and wool fibre can take place in three ways (CEGARRA et al., 1999).

(1) A saline bond is formed due to the presence of sulphonic groups in the dye molecule.

(2) Bond formations due to secondary valences such as hydrogen bridges, Van der Waals forces etc.

(3) Covalent bond formation between fibre reactive sites and dye reactive group (Figure 1.17).

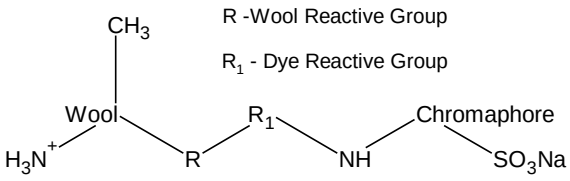


Figure 1.17 The formation of a covalent bond

Reaction pathways (1) and (2) give wools with poorly fixed dyes. For reaction pathway (3) there are two reaction mechanisms that may take place between the wool and the dye. These are nucleophilic substitution and nucleophilic addition reactions (CEGARRA et al., 1999). When using α-bromoacrylamidic dyes both types of reaction can take place as illustrated in Figure 1.18.

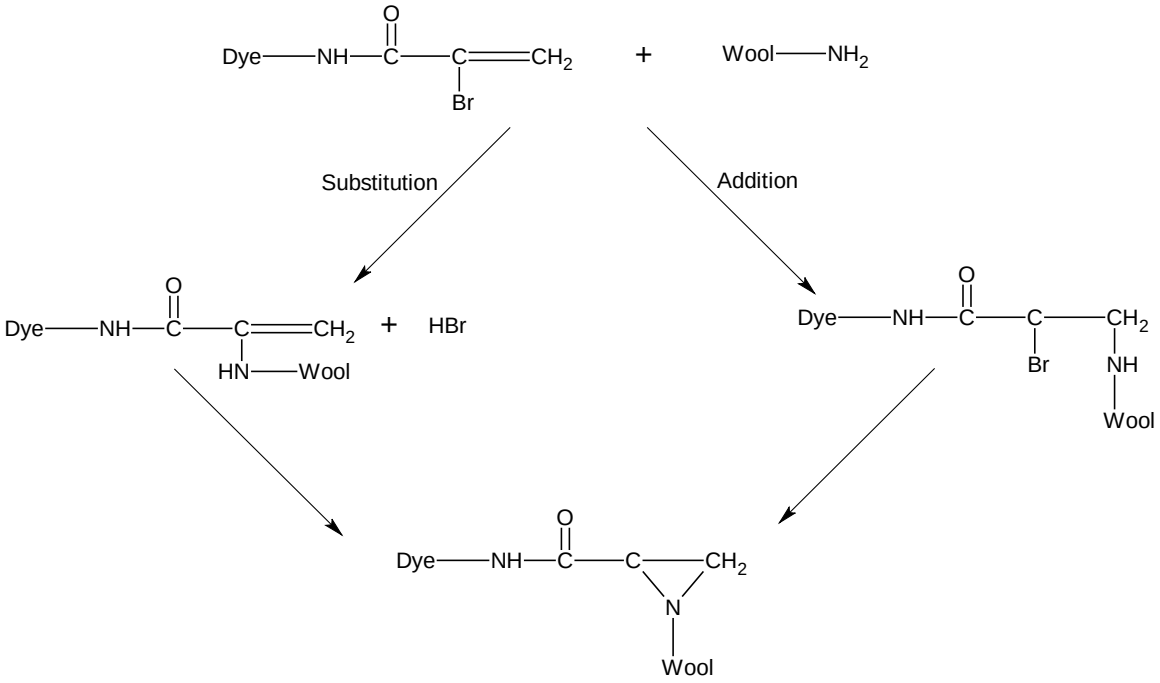


Figure 1.18 Nucleophilic substitution and nucleophilic addition reactions when dyeing wool with reactive dyes

Dyeing with acid dyes

Acid dye liquor is normally composed of a mineral organic acid, the dye, a neutral electrolyte and the fibre. They are all immersed in an aqueous solution, in different proportions according to the processes. These components form liquor made up of an

ion mixture, including the acid hydrogen ions, dye sodium ions, the added neutral electrolyte sodium ions and the anions of the acid, dye and the electrolyte (CEGARRA et al., 1999). When wool is immersed into the acid dye bath, hydrogen ions are absorbed by carboxyl groups of the fibre.

Dyeing baths contains both dye ions and inorganic ions. The latter diffuse more quickly due to smaller molecular dimensions. As a result they are absorbed by the fibre prior to the dye ions (CEGARRA et al., 1999).

Equilibrium is quickly reached and from that moment the fibre absorbs the dye ions (Col^-) which subsequently displace an equivalent quantity of inorganic ions (CEGARRA et al., 1999). The entire process is presented in Figure 1.19.

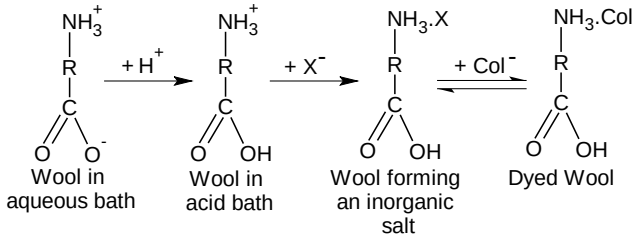


Figure 1.19 Overall process for the acid dyeing of wool (CEGARRA et al., 1999)

1:1 metal complex dyeing theory for wool

1:1 metal complex dyes are soluble complexes that are formed by chromium and azoic type dyes. They dye wool in strong acid liquor (pH 2 with sulphuric acid). It is suggested that there are four types of bonding possible between the dye and the wool fibre (CEGARRA et al., 1999).

1) Dye-SO_3^- ^+H_3N-fibre (in acid solution)
2) Dye-Cr^+ ^-OOC-fibre (in neutral solution)
3) Dye-Cr ←**:**NH_2-fibre (co-ordination)
4) Dye……Fibre (Van der Waals forces)

There is an increased dye adsorption with the addition of acid to the dye bath until a maximum is reached. This is identical to that of acid dyes. Adsorption can be reduced using a lower (neutral) pH as the $–COO^-$ groups combine with protons to give non-dissociated –COOH. Union with Cr^+ is only possible with dissociated carboxyl groups. Reaction 3, co-ordination is a less probable route for reasons relating to the dissociated carboxyl groups. If the pH is lowered further, below the maximum adsorption, the imino groups >NH with weak basic characteristics can protonise to $>NH_2^+$ making coordination with the chromium impossible. Due to this large quantities of sulphuric acid (8% on fibre weight) are used. Under these conditions secondary forces are assumed to influence the affinity of the dye for the fibre, these are Van der Waals forces. Finally, there is the possibility that during the dyeing process the 1:1 metal-complex dye can change to a 1:2 metal complex dye within the fibre (CEGARRA et al., 1999) when they undergo lengthy boiling processes, Figure 1.20 illustrates this.

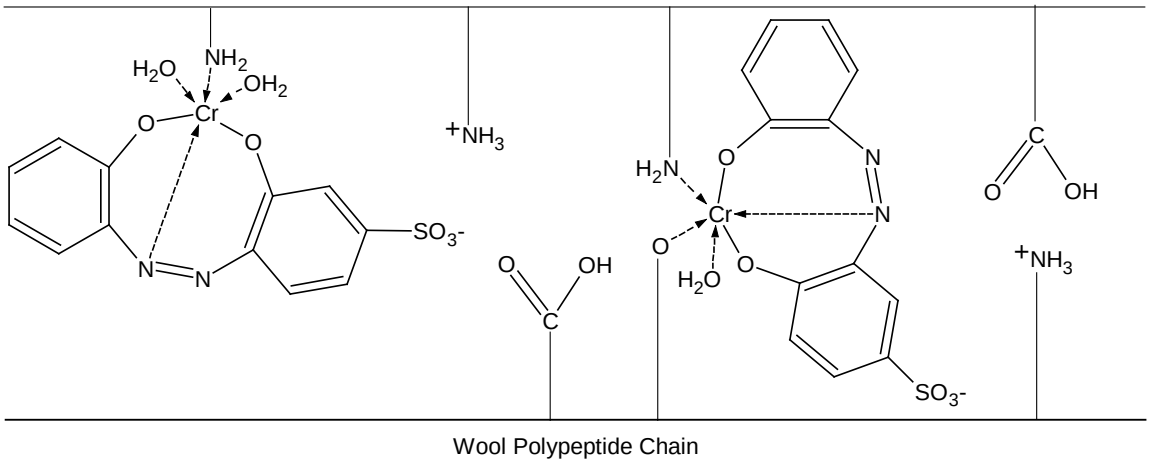


Figure 1.20 Diagram of wool fibre having undergone 1:1 metal complex dyeing

1:2 metal complex dyeing theory for wool

In 1:2 metal complex dyes, the metallic atom has all bonds occupied by the dye so cannot form coordination bonds with wool reactive groups. Due to the negative charge of the dye complex, adsorption is influenced by pH. It is possible that secondary type bonds are established through Van der Waals forces and at times this is the cause of

strong wet fastness. This is due to the dye having large molecular dimensions. Dyeing in neutral liquor with 1:2 metal complex dyes allows two types of bonds to be formed with the fibre (CEGARRA et al., 1999).

1) $Dye^{+}H_3N^{-}$ -- fibre (Ionic bond)
2) Dye…….....fibre (Van der Waals secondary bond)

The dye in the form of free acid is strongly adsorbed by the fibre even at pH 7. This is due to a partially ionic adsorption mechanism in specific sites and another of a solution of solid in solid. In dyes containing sulphonic or carboxyl groups the capacity to form an ionic bond increases. Factors influencing wool dyeing are temperature, pH of liquor, inorganic neutral salts and products of reaction.

1.2.4 Impregnation of wool with metal cations

Experiments have shown wool to be un-shrinkable following treatment with cuprammonium hydroxide, due to reduction in the ability to recover the fibres from deformation (WHEWELL et al., 1959). The reagent reacted rapidly with wool and contraction of the fibres was observed. Copper was not removed by washing with water however immersion in 5% sulphuric acid rendered complete removal. This also allowed contracted fibres to recover their original dimensions. The absorption of copper from copper ammine solutions is dependent on many factors (WHEWELL et al., 1959). These include composition and concentration of reagent, time and temperature of the treatment and the history of the wool. Absorption of copper from solutions of cuprammonium hydroxide, cupri-n-propylamine hydroxide and cupriethylene diamine follow the same trend. At 25^{o}C maximum uptakes of 0.2167 mmol/g wool could be achieved after 2-3 hours of treatment. The length of time for maximum uptake increased as the temperature decreased. In all cases it was observed that there is a rapid initial absorption followed by a much slower rate under dilute solutions (0.0175M). The overall reaction has been expressed in Equation 1 as an exchange (WHEWELL et al., 1959).

$$CuL_4 + 4W \overset{k_1}{\rightleftharpoons} CuW_4 + 4L$$ **Equation 1**

L represents the ligand and W the groups of keratin taking part in the reaction. It is probable that during absorption, intermediates are formed as summarised in the stepwise Equation 2 to Equation 5.

$$CuL_4 + W \rightleftharpoons CuL_3W + L$$ **Equation 2**

$$CuL_3W + W \rightleftharpoons CuL_2W_2 + L$$ **Equation 3**

$$CuL_2W_2 + W \rightleftharpoons CuLW_3 + L$$ **Equation 4**

$$CuLW_3 + W \rightleftharpoons CuW_4 + L$$ **Equation 5**

The stronger the bond between the ligand and metal, the more difficult will be its replacement by groups of keratin.

This work was further discussed by Fukatsu (1988) where it is suggested that depending on pH, both free and dissociated carboxyl groups are present as given in Equation 6 and Equation 7.

$$-COOH + M^{2+} \rightleftharpoons -COOM^{+} + H^{+}$$ **Equation 6**

$$-COO^{-} + M^{2+} \rightleftharpoons -COOM^{+}$$ **Equation 7**

M represents the metal ligand. For the reaction of wool with Cu (II), equilibrium Equation 6 is favoured over Equation 7 at low pH. Equation 6 is influenced by the concentration of the metal cation in the neighbourhood of carboxyl groups. The

equilibrium lays to the far right under high concentrations, therefore, the uptake of Cu (II) ion increases. Under lower concentrations, Equation 6 becomes difficult, thus the uptake is depressed.

Fukatsu (1988) also carried out the same study on both Zn (II) and Ni (II) ions. It was found that the metal ion uptake was three times greater for Cu (II) compared with Zn (II) and Ni (II) when using the same concentration of impregnating solutions. In both of these cases it was found that the equilibrium Equation 7 is favoured.

Recently work has been carried out on the binding of Ag^{+} and Cu^{2+} to chemically modified wools. It was found that unmodified wool absorbed 0.71 and 0.55mmol/g Ag^{+} and Cu^{2+} respectively, and that free carboxyl groups of aspartic and glutamic acid were the main binding sites for both cations at acidic to neutral pH (FREDDI et al., 2001). Factors such as time, temperature, pH and metal concentration were indicated as greatly influencing the rate and extent of metal uptake. Chemical modification of the wool was investigated to improve metal uptake using tannic acid (Appendix 2). Tannic acid is held on to the fibre substrate by weak interactions, no covalent bonds are formed. Modification of the wool with tannic acid enhanced the absorption of both Ag^{+} and Cu^{2+} due to the increased number of binding sites available to give maximum uptakes of 1.4mmol/g for Ag^{+} and 0.70mmol/g for Cu^{2+} at pH 11.4. This was expected as the number of binding sites available increases after modification due to the increased number of available hydroxy groups. Under alkaline conditions nitrogen from amine and peptide groups can also participate in metal coordination. The absorption of metal cations by protein fibres is a reversible process, as the metal cations can be completely desorbed from wool using strong mineral acids. It was found that smaller amounts of metal cations were released from modified wool (3.7% Ag^{+} and 6.4% Cu^{2+}) than unmodified wool (9% Ag^{+} and 40.5% Cu^{2+}).

The optimum conditions for the application of aluminium salts to wool (HARTLEY, 1968b), yielded a maximum uptake of aluminium (0.1086 mmol/g wool) after 48 hours of exposure to 0.2M aluminium sulphate solution (pH 3.25). It was found that fastness of aluminium was poor, and that after washing with water aluminium was eventually

removed from the wool, as aluminium preferred water or hydroxyl ions as ligands rather than the carboxylate or sulphonate groups present on the wool (HARTLEY, 1968b). Temperature studies for scoured, reduced and chlorinated wools showed the aluminium uptake exhibits a maximum at approximately 60°C, 40°C and 40°C respectively. This temperature dependence of uptake suggests that the aluminium was bound to carboxylate ions, as represented by Equation 8 and Equation 9.

$$W - COOH \overset{k_1}{\rightleftharpoons} W - COO^- + H^+ \qquad \textbf{Equation 8}$$

$$W - COO^- + Al(H_2O)_6^{3-} \rightleftharpoons [W - COOAl, xH_2O]^{2+} + (6 - x)H_2O \qquad \textbf{Equation 9}$$

W represents wool and the function k_1 for wool is given by $[W\text{-}COO^-][H^+]/[W\text{-}COOH]$ and like for other carboxylic acids, k_1 for wool will exhibits a maximum with respect to temperature. Carboxylic acids which may be considered as model compounds for wool include acetic acid, glycine and glycyl-glycine which exhibit maximum k_1 values at 22.5°C, 26.0°C and 51.5°C respectively. A maximum in the concentration of free carboxylate ions would lead to a maximum binding of aluminium (HARTLEY, 1968b).

When wool is dyed using a chrome mordant, (a substance used in dyeing to fix the dye, forming an insoluble coloured compound in the fibre), the chromine species in wool was found to be Cr (III). A mordant substance is used for setting dyes which are either inherently colloidal or produce colloids. Mordant substances can be acidic or basic. For wool exposed to Cr (III) solutions for 24 hours at 60°C (pH 2.5), it was found that after initial washing no further Cr (III) was removed from the fibre by water or after boiling in potassium dichromate. Cr (III) cations were not displaced from wool by soaking in neodymium (III) or aluminium (III) solutions with only trace amounts of Cr (III) displaced, even after 7 days (HARTLEY, 1968a). This suggested that Cr (III) was bound covalently to wool. Cr (III) uptake was influenced by the salt used, temperature and pH, with maximum uptake (0.3071 mmol/g wool) using chromium (III) sulphate at 80°C and pH of 2.5. The results showed that Cr (III) was normally bound to carboxyl groups in wool and that the amino groups were not involved. When Cr (III) coordinates to wool, the negative ligands present in the Cr (III) complex in solution are retained and

water molecules are displaced (HARTLEY, 1968a). This observation is consistent with Cr (III) reacting with wool by the S_N1 mechanism given in Figure 1.21.

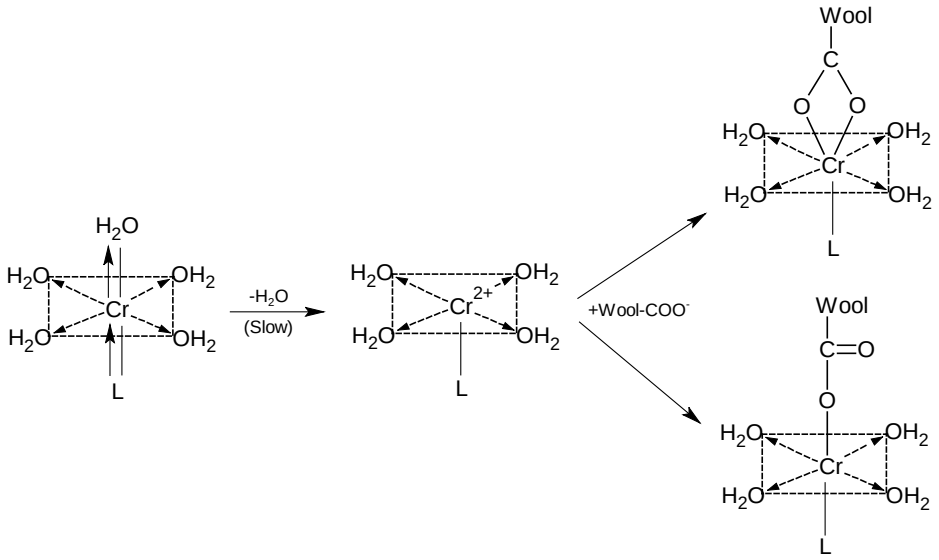


Figure 1.21 The S_N1 reaction of Cr (III) with wool (HARTLEY, 1968a)

Wool has also been investigated for the uptake of zirconium chloride. The wool and Zr (IV) were equilibrated under acidic conditions to assist binding. Adjustments were carried out to raise the pH until precipitation of excess zirconium in the form ZrO_2, still leaving Zr(IV) bound to the fabric. Uptake was determined by ashing, thus converting the Zr(IV) on the fabric to ZrO_2. It was found that the maximum uptake 1.92% ZrO_2 was achieved using 0.015M zirconium chloride in 0.14M H_2SO_4 at 70^oC (pH 2.0-2.6). This uptake was irreversible. Uptakes were found to be much lower at 25^oC compared with 70^oC, suggesting swelling of the wool at higher temperatures to either accommodate more ZrO_2 or present more binding sites due to increased surface area (LAURIE, 1966). Studies using wool pre-swollen in formic acid followed by impregnation showed the uptake by wool to increase to 11.5% ZrO_2 determined by ashing. However, the addition of a swelling agent weakens the wool.

Initial studies have been carried out for the impregnation of wool with aqueous solution of titanium (III) under a nitrogen atmosphere, to avoid premature oxidation of Ti (III) to Ti (IV) (LAURIE, 1968). The effects of temperature, time, pH and addition of neutral salts during impregnation have been examined to determine their influence on final

Ti(III) content (evaluated by ashing). It was found that uptake increased with increasing temperature and the addition of sodium sulphate, but was fairly independent of pH over the range pH 1.5-3.0. Overall uptakes were found to be three times greater than those for Zr(IV) for similar impregnation concentrations (2.1% TiO_2 at 80^oC for 2 hours and 0.03M Ti(III) solution). The use of a nitrogen atmosphere is not commercially attractive therefore it was found at higher temperatures (80-100^oC) with shorter reaction times it could be dispensed with. This did not cause any substantial loss of Ti(III) uptake (LAURIE, 1968).

Extensive research has been carried out investigating the removal of mercury from industrial effluents using wool. Uptakes were determined using cold vapour atomic adsorption for wool exposed to 100ppm mercury chloride (II) solution for 2 hours at ambient temperature. 36ppm mercury was sorbed to the wool, however with the addition of a detergent (Diversey H.D.) mercury sorption increased to 90ppm (LAURIE and BARRACLOUGH, 1979). Factors found to influence uptake were temperature, pH and wool liquor ratio. Increased temperature allows for greater uptakes in a shorter reaction time. The optimum pH was found to be in the range of pH 3-5. At neutral pH there was a marked inhibitory effect by the chloride ion on mercury sorption (LAURIE and BARRACLOUGH, 1979), and that the concentration of chloride ion had varied effects on the mercury (II) uptake. Highest uptakes (~90%) were achieved using wool (0.5g), $HgCl_2$ (50mls, 100ppm), pH6 and 25^oC with the addition of 0.5mM NaCl, uptakes reduced with increasing concentration of NaCl.

A new stable chelating material has been prepared by loading hydrogen peroxide bleached wool with mordant yellow 10 (VLADESCU et al., 2004). The sorption capacity for Fe (III) and the effect of pH on Fe (III) absorption and removal was investigated. Fe (III) sorption was determined as 24mmol/g wool but all of the Fe (III) retained by this modified wool could be removed by elution with 1M HCl.

1.3 Catalysis

1.3.1 The use of wool as a support for an active catalyst site

Researchers in China have prepared a wool catalyst containing Pt by the reaction of wool with $H_2PtCl_6 \cdot 6H_2O$ in ethanol solution. This catalyst has been used in the asymmetric hydrogenation of aliphatic and aromatic ketones to corresponding chiral alcohols under mild conditions (YUAN et al., 1999). The structure of wool-Pt catalyst is shown in Figure 1.22. In the asymmetric hydrogenation of 3-methyl-2-butanone it was found that an optical yield of 100% alcohol could be achieved when the Pt content of wool was 0.116mmol/g, and was maintained over two cycles.

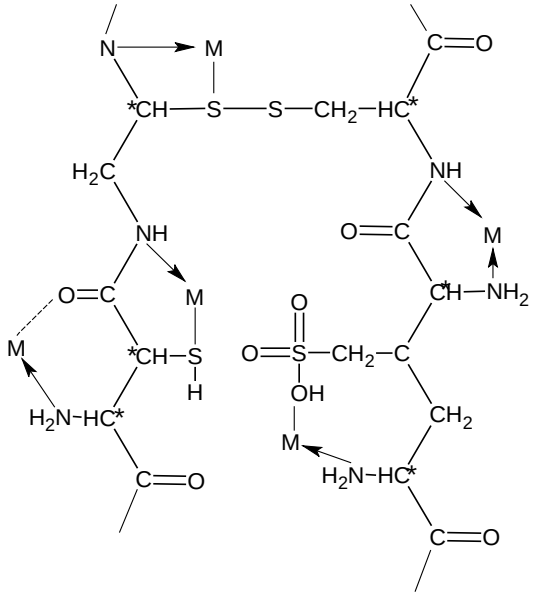


Figure 1.22 The structure of the wool-M complex (M = $H_2Pt_XCl_Y$, $PdCl_X$, $RhCl_X$, $Pd/FeCl_X$ or OsO_4)

Yin et al. (1999) found that wool-Pd complex was able to catalyse the asymmetric hydrogenation of diacetone alcohol and 3-methyl-2-butanone. The wool-Pd complex was prepared using wool (0.1g), $PdCl_2 \cdot 2H_2O$ (0.03 mmol) and ethanol (5ml) stirred and refluxed for 3 hours. The structure of the wool-Pd complex is given in Figure 1.22. It was found that optical yields of 100% could be achieved for the hydrogenation of diacetone alcohol and 3-methyl-2-butanone. This was maintained for two cycles when the Pd content of wool was 0.30mmol/g. It was suggested that other prochiral

compounds could be used. Similar to the wool-Pt catalyst the wool-Pd was easy to prepare and could be reused without appreciable change in optical catalytic activity.

Wool-Pd has also been used to catalyse the asymmetric hydration of alkenes. It was found that the N, S and O atoms in wool can coordinate or connect the metal ion by ionic bonds to form chiral wool-metal complex (XUE et al., 2004). Optical yields of the alcohol obtained during catalysis were 83.2% for 1-octene and 75.6 for 1-decene for a wool catalyst with a Pd content of 0.1mmol/g. The optimum reaction time in both cases was 24 hours. When the catalyst was used several times, the product and optical yields only slightly decreased (XUE et al., 2004). It was concluded that the wool-Pd complex was an economical and effective catalyst for asymmetric hydration of alkenes.

A rhodium complex of wool (wool-Rh) see Figure 1.22 has been prepared from wool (0.1g) and $RhCl_3.3H_2O$ (0.01 mmol) in ethanol (5ml) stirred and refluxed for 12 hours (HE et al., 2003). It has been used to catalyse the asymmetric hydrogenation of 2-methyl-furan in non-aqueous solvent under mild conditions. It was found that the maximum optical yield of 76.9% was achieved with a Rh content of 0.08mmol/g. Temperature and reaction time also influenced the catalytic activity with the optimum being at 28^{o}C and 24 hours respectively. Catalyst stability was also evaluated by recovery and reuse. The catalyst was used five times in total without appreciable change in its catalytic activity.

A wool-supported palladium-iron complex (wool-Pd-Fe) has been developed and used in hydration of alkenes (JIA et al., 2003). It was prepared by the reaction of wool with $PdCl_2{\cdot}2H_2O$ and $FeCl_3{\cdot}6H_2O$ in ethanol. The structure of the wool-Pd-Fe complex is given in Figure 1.22. Table 1.4 summarises the results obtained for the hydration of alkenes catalysed by the wool-Pd-Fe complex. It was found that the catalyst was very selective and stable. The hydration results were all affected by the Pd/Fe molar ratio, reaction temperature and time. In the hydration of allylbromide the Pd/Fe molar ratio was best at 0.33, at 95^{o}C for 24 hours. The catalyst could be reused seven times without change in catalytic activity.

Table 1.4 Results obtained for the hydration of alkenes catalysed by the wool-Pd-Fe complex

Alkene	Alcohol	Reaction Time (h)	Yield of alcohol (%)
Allylbromide	1-Bromo-2-propanol	24	95.0
Allylchloride	1-Chloro-2-propanol	24	87.5
Allylamine	1-Amino-2-propanol	24	90.6
Acrylonitrile	Lactonitrile	28	75.3
Cyclohexane	Cyclohexanol	36	98.2

Condition: Catalyst, wool-Pd-Fe (Pd/Fe molar ratio, 1/3; Fe, 0.10 mmol/g),.0.1g; substrate, 0.5ml; water, 2ml; butyl ether, 3ml; phenol, 0.1g; 95 ^{o}C, 1atm N_2.

Finally work has been carried out involving the asymmetric dihydroxylation of allylamine catalysed by wool-osmium tetroxide complex (wool-OsO_4). The catalyst was prepared by mixing wool pieces in a solution of OsO_4 for 24 hours at 60^{o}C under a nitrogen atmosphere. OsO_4 solutions were prepared by dissolving 0.5g in reagent grade tert-butyl alcohol (100ml) followed by the addition of several drops 70% t-BuOOH. A maximum optical yield of 83.7% was achieved for allylamine when the OsO_4 content was 0.0588mmol/g with a reaction time of 24 hours. It was found that the wool-OsO_4 complex was stable and could be reused three times without any remarkable change in optical activity (MIAO et al., 2003). The chemical structure of the wool-OsO_4 complex is given in Figure 1.22.

1.3.2 Fenton's Reagent

The combination of hydrogen peroxide and Fe (II) ions is known as Fenton's Reagent, and it is classified as one of the Advanced Oxidation Processes (AOP). Such processes are being developed to solve environmental problems related to the generation of non-biodegradable and toxic wastes (ARIS, 2004). In recent years such processes have been proposed for the effective destruction of organic constituents in wastewater (STALIKAS et al., 2001).

Principles of Advance Oxidation Processes

AOPs are a category of chemical oxidation process which generate and utilise hydroxyl radicals ($^{\cdot}OH$). It is known that $^{\cdot}OH$ is the second most reactive oxidising agent which is common after fluorine. Hydroxyl radicals have an oxidation potential of 2.80V whereas this is 3.03 V for fluorine (LEGRINI et al., 1993).

The reactions of $HO^{\cdot}$ with various materials have been reported by Legini et al. (1993) which can result in the production of carbon dioxide and/or water. These can be classified into four types.

1. Hydrogen abstraction.
2. Electrophilic addition.
3. Electron transfer.
4. Radical-radical reactions.

Hydrogen abstraction is the most common of the mechanisms. This is where hydrogen is abstracted from an organic to form organic radicals ($R^{\cdot}$) and water (ARIS, 2004) as given in Equation 10 under acidic conditions. The organic radicals can be converted to peroxyl radicals ($RO_2^{\cdot}$) in the presence of O_2 (Equation 11).

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \qquad \textbf{Equation 10}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad \textbf{Equation 11}$$

Electrophilic addition is normally related to the addition of $HO^{\cdot}$ to organic π-systems as this can also lead to the formation of organic radicals (ARIS, 2004). This is demonstrated in Equation 12. In general pH is acidic or neutral depending on the reagents used and the reaction may require heat or light. When an electron transfers to $HO^{\cdot}$, forming the hydroxide ion (HO^{-}), this is known as electron transfer (Equation 13).

$$HO^{\bullet} + PhX \rightarrow HOPhX^{\bullet} \qquad \textbf{Equation 12}$$

$$HO^{\bullet} + RX \rightarrow RX^{\bullet +} + HO^{-} \qquad \textbf{Equation 13}$$

Radical-radical reactions take place at higher concentrations of $HO^{\cdot}$. This allows $HO^{\cdot}$ to react with another $HO^{\cdot}$, other radicals or even H_2O_2 to form water and/or less reactive radicals such as hydroperoxyl radicals, $HO_2^{\cdot}$ (ARIS, 2004). These reactions are summarised in Equation 14 and Equation 15.

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \qquad \textbf{Equation 14}$$

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad \textbf{Equation 15}$$

Types of Advanced Oxidation Processes (AOPs)

There are several techniques that can be used in generating $HO^{\cdot}$. In general, these comprise of a reaction between an oxidant with a co-oxidant or a catalyst. AOPs are broadly classified into two main categories, homogeneous or heterogeneous. Homogeneous catalysis is where the catalyst is in the same phase as the reactants, whereas heterogeneous catalysis is where the catalyst is in a different phase (ie. solid, liquid and gas, but also oil and water) to the reactants. This provides a medium or surface on which the reaction may take place. Table 1.5 reports common AOPs grouped by oxidant used (ARIS, 2004).

Table 1.5 Common Advanced Oxidation Processes grouped by oxidant

Reaction Phase	Main Oxidant	Processes
Homogeneous	O_3	O_3/high pH; O_3/H_2O_2; O_3/UV; O_3/H_2O_2/UV
	H_2O_2	H_2O_2/UV; H_2O_2/Fe^{2+}; H_2O_2/Fe^{3+}; H_2O_2/Fe^{2+}/UV; H_2O_2/Fe^{3+}/UV; H_2O_2/Fe^{3+}-oxalate
Heterogeneous	O_3	O_3/solid catalyst
	H_2O_2	H_2O_2/iron oxide
	None (termed as photocatalyst)	UV/TiO_2; UV/TiO_2/O_2; UV/TiO_2/H_2O_2; UV/metal oxides

Comparison of Advanced Oxidation Processes (AOPs)

Many studies have been conducted to compare AOPs. Table 1.6 summarises the advantages and disadvantages of selected AOPs (NAMKUNG, 2002).

Table 1.6 Comparison of advantages and disadvantages of selected AOPs

Process	Advantages	Disadvantages	References
UV/O_3	• Selectivity of ozone oxidation • Economic at high pH (>7) for wastewater • Suitable for drinking water disinfection	• Low yield of $HO^{\bullet}$ generation • Dependence on solubility of O_3 in water and mass transfer limitations • Needs 253.7nm light	(LEGRINI et al., 1993), (PEREZ et al., 2002a), (MUNOZ et al., 2005)
UV/H_2O_2	• High yield of $HO^{\bullet}$ generation • Suitable for drinking water disinfection • Infinite solubility of H_2O_2 • No need for post-treatment	• Needs UV-C light • Limitation of the chemical oxidation rate by the generation rate of $HO^{\bullet}$ • Needs maintenance of O_2 concentration	(LEGRINI et al., 1993), (PEREZ et al., 2002a), (MUNOZ et al., 2005)
UV/Fe^{2+} $(Fe^{3+})/H_2O_2$	• High yield of $HO^{\bullet}$ generation • High reactivity with the treatment of most organic pollutants • Can be applied to high strength wastewaters • Use of near UV light and solar radiation	• Should be pH < 4 • Sludge production • Needs UV and few particulates	(LEGRINI et al., 1993), (MUNOZ et al., 2005), (PIGNATELLO, 1992)
Ultra Sonic $/O_3$	• High oxidation efficiency • High reactivity with the treatment of most organic pollutants • Suitable for drinking water disinfection	• High cost • Little data	(WEAVERS and HOFFMANN, 1998), (WEAVERS et al., 1998)
Electron Beam	• High oxidation efficiency • High reactivity with the treatment of most organic pollutants • No limitation with respect to waste characteristics • Complete mineralization	• High cost • Safety of equipment	(GEHRINGER and ESCHWEILER, 1999), (GEHRINGER and FIEDLER, 1998), (SAMPA et al., 2004), (DUARTE et al., 2002)

Table 2.6 Continued

Process	Advantages	Disadvantages	References
H_2O_2/O_3	• Cheap process • Suitable for drinking water disinfection • No need for post-treatment	• Low efficiency • Needs high pH • Dependence on physical mixing of H_2O_2 with O_3	(PAPIC et al., 2006), (WU et al., 2006)
Fe^{2+}/H_2O_2 (Fenton)	• Cheap process • Relative stability of chemicals • Easy to control • High flexibility in a process design • Examples of real-scale plants	• Needs a large amount of ferrous species • Should be pH < 4 • Sludge production	(PEREZ et al., 2002a), (ESPRO et al., 2000), (KANG et al., 2002)
$UV/TiO_2/O_2$ (H_2O_2)	• Treatment of most organic pollutants • No need for post-treatment • Stability and non-toxicity of the catalyst • Suitable for drinking water disinfection	• Slow oxidation • Needs separation of the catalyst • Difficulty in treatment of high strength wastewaters	(PEREZ et al., 2002a), (GULYAS et al., 1994)
Iron oxide/H_2O_2	• Cheap process • Non-toxicity of iron oxides • Treatment of contaminated soils and groundwater	• Low oxidation efficiency • Difficulty in treatment of high strength wastewaters	(ENSING et al., 2003)

Other studies have been performed to compare efficiencies of AOPs. These were based on chemical and energy costs. It was found that Fenton Reagent systems (FR, Fenton-like and photo-Fenton) had better degradation capabilities than other processes (ARIS, 2004). It was also reported that FR was the most economical process on the basis of cost per kg of Total Organic Carbon removed.

Principles of Fenton's Reagent Oxidation

The mechanistic chemistry of the FR process has been of great interest to many researchers. Since its first discovery, two main mechanisms have been accepted. It was suggested by Bray and Gorin (1932) that the ferryl ion (Fe (IV) as FeO^{2+}) was formed

(Equation 16). The involvement of HO· was suggested by Haber and Weiss (1934) two years later (Equation 17).

$$H_2O_2 + Fe^{2+} \rightarrow FeO^{2+} + H_2O$$ **Equation 16**

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$$ **Equation 17**

Direct experimental evidence for the formation of FeO^{2+} has not been obtained although the idea has been supported by many investigators. It has been generally accepted that this gives rise to the generation of HO· (ARIS, 2004). The Haber-Weiss pathway is more favoured by researchers as the formation and involvement of HO· has been well established through experimental observations.

The consecutive reactions given in Equation 18 to Equation 24 relate to the radical-chain mechanisms (BARB et al., 1951) and have been widely accepted in literature.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$$ **Equation 18**

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$$ **Equation 19**

$$HO^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}$$ **Equation 20**

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^{+} + HO_2^{\bullet}$$ **Equation 21**

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2$$ **Equation 22**

$$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + HO^{\bullet}$$ **Equation 23**

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+}$$ **Equation 24**

When an organic substrate (RH) is present, the primary product of oxidation would be the organic radical, $R^{\cdot}$. This has predominantly reducing properties and can be consumed through reactions with H_2O_2, Fe^{3+} and O_2 as shown in Equation 25 to Equation 28.

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet} \quad \textbf{Equation 25}$$

$$R^{\bullet} + H_2O_2 \rightarrow ROH + HO^{\bullet} \quad \textbf{Equation 26}$$

$$R^{\bullet} + Fe^{3+} \rightarrow PRODUCT + H^{+} + Fe^{2+} \quad \textbf{Equation 27}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad \textbf{Equation 28}$$

The peroxo-organic radical formed in Equation 28 can participate in another series of reactions (UTSET et al., 2000). This is demonstrated in the equations given below.

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad \textbf{Equation 29}$$

$$RO_2^{\bullet} + H_2O \rightarrow ROH + HOO^{\bullet} \quad \textbf{Equation 30}$$

$$RO_2^{\bullet} + H_2O_2 \rightarrow RO^{\bullet} + H_2O + O_2 \quad \textbf{Equation 31}$$

The FR process when initiated by the Fenton reaction (Equation 18) can be divided into two stages, where the initial stage is faster than the later stage. During the first stage $HO^{\cdot}$ is produced quickly by the Fenton reaction, which rapidly decomposes pollutants. As the initial Fe^{2+} is consumed, it transforms into Fe^{3+}. This is the second stage of the FR system and the chain reactions are propagated by the Fenton-like reaction given in Equation 21. The Fenton-like reaction gives rise to the generation of $HO_2^{\cdot}$ and regenerates the Fe^{2+} ion allowing further reaction. Since the Fenton-like reaction is slower and $HO_2^{\cdot}$ is a less reactive species compared with $HO^{\cdot}$, the degradation process in the second stage is much slower.

When the FR process is initiated by the Fenton-like reaction as given in Equation 21, the reaction is slower from the start. However, as the reaction precedes more Fe^{3+} is converted to Fe^{2+}, hence reactions become faster. The extent of the overall degradation is similar to that with the Fenton reaction.

Factors affecting the efficiency of Fenton's reagent

Although the FR process is simple it may be affected by many factors. The most important factors that have been well documented and include (ARIS, 2004);

1. pH
2. H_2O_2 dosage
3. Fe^{2+} dosage
4. Temperature
5. Characteristics of pollutants
6. Dissolved oxygen (DO)
7. Light

pH

The optimum pH for the system is generally between pH 2.5 and pH 3.5 for un-complexed Fe (II) (PIGNATELLO, 1992). This narrow pH requirement is attributed to the sensitivity of Fe^{2+} or Fe^{+3} and H_2O_2 to pH. It is anticipated that the lower efficiency of the process at pH less than 2.5 is due to the formation of complex iron species which react more slowly with H_2O_2 hence producing less $HO^{\cdot}$. At high pH there is the formation of Fe (II) complexes in solution which inhibits radical formation. In addition to this the precipitation of ferric oxyhydroxides (Fe_2O_2-nH_2O) contributes to the slower reaction as Fe (III) is removed from the reaction, thus less cycling to Fe (II) occurs. Hydrogen peroxide readily decomposes to water and oxygen at high pH. When using complexed Fe (II) it is possible to use the Fenton's process at pH 2.3 to greater than pH 7.0 (YURKOVE et al., 1999). The system would however require optimisation in relation to the target pollutant. Both complexed and un-complexed Fe (III) is effective

in the pH range 2.5-7. However, the optimum has been found to be between pH 2.5 and pH 5.0 (PARK et al., 2006; GEORGI et al., 2006).

Hydrogen peroxide dosage

The required dosage of H_2O_2 can be affected by the type of pollutants and the H_2O_2 / Fe ratio. It has been suggested that preliminary studies be conducted to identify the required dosage of peroxide to be applied to wastewaters and/or specific pollutant targets.

In terms of degradation it has generally been observed that the efficiency of the FR process increases with increasing H_2O_2 dosage where there is sufficient iron present. In some situations, when using a higher H_2O_2 concentration there comes a point where no further enhancing effect is observed (PIGNATELLO, 1992; KONG et al., 1998), possibly due to the scavenging effect of H_2O_2 producing $HO_2^{\cdot}$ which is less reactive than $HO^{\cdot}$ (Equation 19). Alternatively, it could be through recombination of $HO^{\cdot}$ due to its excessive concentration, thus reproducing H_2O_2, Equation 22. In the longer term, a higher initial peroxide dosage has been shown to increase the extent of removal and improve the level of mineralization. It is also possible that dosing could be used throughout the reaction.

Iron dosage

An increase in iron dosage has been found to improve the degradation rate of the FR process. However, similar to H_2O_2 dosage there comes a point where further dosage increase results in a reduction in efficiency. This is probably due to the scavenging of radical by Fe^{2+} as shown in Equation 20 (KANG et al., 2002; KONG et al., 1998). The effect of Fe^{2+} has also been observed to be dependent on other factors such as H_2O_2 dosage, type of iron used and reaction time.

In the case of dyes it has been found that an increased Fe^{2+} dosage gave better decolourisation than when using Fe^{3+}. The reaction with higher Fe^{2+} dosage proceeded faster in the first few minutes (PEREZ et al., 2002b). However, as the reaction progressed the influence of increased Fe^{2+} became less significant. With longer reaction

times, the overall degradation and mineralization was found to be independent of the iron oxidation state.

Temperature

Many different optimum temperatures have been reported from 25-70^{o}C. The majority of studies suggest that FR and photo-Fenton reactions are more effective at higher temperatures (PEREZ et al., 2002a; PEREZ et al., 2002b). This however is not conclusive. The best operating temperature seems to depend on the other operating conditions involved in the process.

Characteristics of pollutants

The characteristics of pollutants or waste waters to be treated have an impact on the efficiency of the FR system. Many system factors are dependent on the concentration of such pollutants, their structures and the presence of $HO^{\cdot}$ scavengers. Factors which may be affected are dosage of reagents, reaction time, and percentage of removal.

General observations reported were that increased pollutant concentration would reduce the degradation rate and extent of pollutant removal. Structurally, unsaturated compounds degrade faster than saturated compounds. The rate of degradation has been found to be slower for aliphatic or cyclic organic substances compared with aromatic compounds.

Some scavengers may reduce the degradation rate by complexing with iron. Others may react with $HO^{\cdot}$ to form less reactive radical species. The significant concentrations of typical scavengers have been reported by Namkung (2002) and are given in Table 1.7.

Table 1.7 Scavengers typically found in water and wastewater

Scavenger	Significant Concentration	Remarks
Chloride (Cl^{-})	> 1000 mg L^{-1}	Strong effect at pH< 5
Nitrite (NO_2^{-})	> 10 mg L^{-1}	
Carbonates (HCO_3^{-}/CO_3^{2-})	> 300 mg L^{-1}	Strong effect at pH > 7
Sulphites (SO_3^{-})	> target pollutant	
Sulphides (S^{2-})	> target pollutant	

Dissolved oxygen

Many studies have shown a rapid depletion of dissolved oxygen (DO) concentration at the start of the Fenton's Reaction (FR) process followed by increased DO concentration as the process progresses (BUDA et al., 2003). It is suspected that the decrease in concentration is due to the reaction of O_2 with intermediate organic radicals (a combination of Equation 28 and Equation 30). This is desirable for completion of the oxidation process. The evolution of O_2 in the latter stages of the FR process is thought to be due to catalytic reactions of H_2O_2 as described in Equation 32.

$$2H_2O_2 \xrightarrow{Fe^{2+/3+}} O_2 + 2H_2O \qquad \textbf{Equation 32}$$

It has been observed that the presence of O_2 in the FR system improves efficiency. This supports the participation of DO in the reactions as discussed previously (Equation 29), thus promoting the degradation process.

Light

Different forms of light source have been tested on FR systems, including sunlight, and have been shown to enhance the process. The overall degradation and mineralization rates of Fenton and Fenton-like reactions were found to improve under irradiation (PEREZ et al., 2002a, PIGNATELLO, 1992). The main mechanism for photo-Fenton (FR + UV light) has been based on the photo-reduction of Fe^{3+} (SUN and PIGNATELLO, 1993). Additional $HO^{\cdot}$ radicals are produced by the photo reaction and the subsequent Fenton reaction (in the presence of H_2O_2) is enabled by the regeneration of Fe^{2+}.

<u>Main advantages of Fenton's reagent processes</u>

There are three main advantages. Firstly $HO^{\cdot}$ radicals react rapidly with organic substances. Such radicals have been shown to react with a variety of compounds in aqueous solutions and waste waters (CASERO et al., 1997). These include;

a) Alcohols (KUZNETSOVA et al., 2004),
b) Ethers (AL ANANZEH et al., 2006; BERGENDAHL and THIES, 2004; BURBANO et al., 2005; HULING et al., 2005; XU et al., 2004),
c) Dyes (KANG et al., 2002; BAE et al., 2004; HSUEH et al., 2005; BALDRIAN et al., 2006; TANG et al., 2005),
d) Phenols (KAVITHA and PALANIVELU, 2004; LEE et al., 2006; NOORJAHAN et al., 2005; MARTINEZ et al., 2005),
e) Pesticides (CATASTINI et al., 2002),
f) Polycyclic Aromatics (LEE et al., 2002; FLOTRON et al., 2005) etc.

Secondly, reagent compounds are environmentally friendly and are easy to handle. The final decay products, water, oxygen and ferric hydroxide introduce no further pollution. Finally, hydrogen peroxide has been used for industrial wastewater treatment to minimize the chemical oxygen demand. The additional cost to the process due to the introduction of ferrous iron is quite low; however consideration must be given to the sludge production when using this process. It has been identified that for the treatment of wastewaters, dyes and phenolic compounds are considered model pollutants.

Degradation of dyes using Fenton Processes

It has been well established that wastewater from the textile dyeing industry is characterised by high temperature, pH, colour and chemical oxygen demand (COD) (BAE et al., 2004). The COD in dyeing wastewaters contain refractory, toxic and high molecular weight compounds, and therefore presumed to be very resistant to microbial degradation. The Fenton process is known for its removal of colour and recalcitrant organics. Kang et al. (2002) reported that for synthetic textile wastewater containing poly vinyl alcohol and a reactive dyestuff, the colour and COD could be removed by oxidation with $HO^{\cdot}$ radical and Fe^{3+} coagulation respectively. The predominant reactions used in the Fenton process for the treatment of dyeing wastewater were quantitatively evaluated. It was found that the soluble chemical oxygen demand (SCOD) and colour removal efficiencies by ferric coagulation were 60.8% and 62.0% respectively. The efficiencies were 67.7% (SCOD) and 84.7% (colour) by Fenton

oxidation. From this it was estimated that one quarter of the colour removal and approximately one tenth of the SCOD removal in the process was achieved by Fenton oxidation. As coagulation was found to be an important mechanism for the dyeing wastewater treatment process, optimisation was carried out. The wastewater was pre-treated using ferric or ferrous ion before Fenton oxidation. This produced 72% removal of SCOD and 91% removal of colour in total. Without pre-treatment, the removal efficiencies were 68% (SCOD) and 90% (colour). In both cases 2mM of Fe^{2+} and 2mM of H_2O_2 were used, after coagulation with 150mg/l ferrous ion. The removal efficiencies were very similar when comparing Fenton oxidation only and Fenton oxidation after coagulation with 150mg/l ferric ion, (76.5% SCOD and 93% colour removal). At low pH most of the reaction is Fenton, at neutral pH most of the reaction is coagulation/precipitation.

Hseuh et al. (HSUEH et al., 2005) studied the degradation of azo dyes using low iron concentration Fenton and Fenton-like systems. The azo dyes used in the study were Reactive Red 2 (CI 18200), Reactive Black 5 (CI 20505) and Acid Orange 10 (CI 16230). The effects of pH, Fe^{3+} dosing and H_2O_2 dosing were investigated. When adopting a Fe^{2+}/H_2O_2 or Fe^{3+}/H_2O_2 system the optimum pH was found to be between 2.5 and 3.0 for both reactions. Table 1.8 displays the results when investigating the effect of Fe^{3+} dose, where the optimum dose was found to be between 1 and 10ppm. However, there was very little difference when using 1ppm and no enhancement of the overall reaction rate was achieved when using 10ppm Fe^{3+}. Initially the reaction proceeds faster when using 10ppm Fe^{3+}. It was concluded that the ratio of Fe to H_2O_2 ranges from 1:10 and 1:100 (ppm).

Table 1.8 The effect of Fe^{3+} dose on the decolourisation of dye

Fe^{3+} Dose (ppm)	**% Decolourisation (10mins)**	**% Decolourisation (60mins)**
0.1	5	13
1.0	22	95
5.0	52	96
10.0	67	97

$[H_2O_2]$ = 100 mg/l, pH = 2.5, Fe^{3+} = Ferric nitrate dosage.

In order to reduce sludge production, 1ppm Fe^{3+} was used for the remaining investigations. In further studies, Hseuh et al. (2005) found that as the H_2O_2 concentration increased from 20-200 mg/l, the decolourisation of dye became enhanced. At the higher H_2O_2 concentrations more Fe^{3+} is converted to Fe^{2+} and $HO^{\cdot}$ radicals are formed. However, with concentrations greater than 200 mg/l, the degradation rate decreases. Table 1.9 summarises the effect of H_2O_2 dosage on the decolourisation of dye.

Table 1.9 Effect of H_2O_2 dosage on the decolourisation of dye

H_2O_2 dose (mg/l)	**% Decolourisation (30mins)**
20	22
100	40
200	54
350	45
500	34

System = Fe^{3+}/H_2O_2, [Fe^{3+}] = 1 mg/l, pH = 3.0

It is known that reaction intermediates can form during the oxidation of azo dyes, some of which may be long-lived and more toxic than the parent compounds. Therefore, the degree of mineralization was determined using TOC removal ratios. Using the same reaction conditions as when evaluating dye decolourisation, the TOC removal ratios were found to be 40% after 480 minutes of reaction indicating that mineralization is quite slow.

Baldrian et al. (2006) investigated the use of heterogeneous catalysis by mixed iron oxides for the decolourisation of synthetic dyes (including Bromophenol blue, Chicago Sky Blue (CI 24410) and Naphthal Blue Black (CI 20470). They evaluated the effects of catalyst loading, the decomposition of hydrogen peroxide and the effect of pH on decolourisation. It was found that when the catalyst content was 25 mg/l the percentage decolourisation was greater. Four catalysts were evaluated for ~17 hours and the results are displayed in Table 1.10.

Table 1.10 Results for the percentage decolourisation of dye with respect to catalyst used

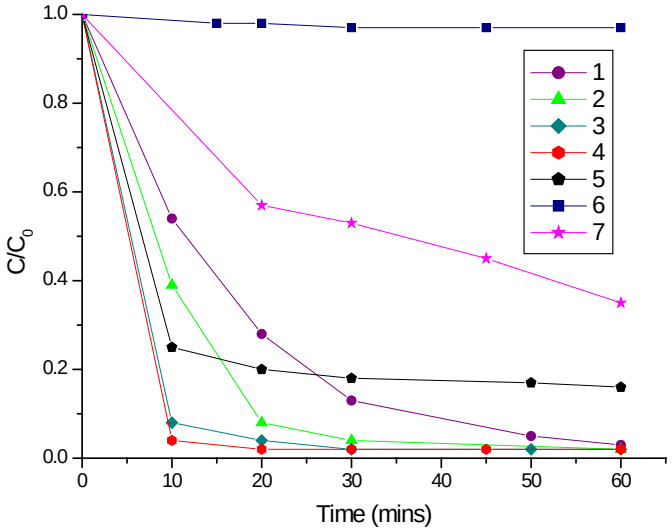
Catalyst Used	% Decolourisation (1000mins)
$CoO{\cdot}Fe_2O_3$	95
$CuO{\cdot}Fe_2O_3$	91
$FeO{\cdot}Fe_2O_3$	88
$MnO{\cdot}Fe_2O_3$	78

$[H_2O_2]$ = 100mM, [Chicago Sky Blue Dye, CI 24410] = 50 mg/l, catalyst content = 25 mg/l

All hydrogen peroxide was decomposed within 2 and 24 hours depending on the catalyst used. The highest rate of decomposition was observed in the initial minutes of reaction. The decomposition of hydrogen peroxide was accompanied by the production of hydroxyl radicals, with the highest concentrations being detected between 10-30 minutes of reaction depending on the catalyst type. $CuO{\cdot}Fe_2O_3$ produced the highest amount of hydroxyl radicals, 0.85 (arbitrary units), whereas $FeO{\cdot}Fe_2O_3$ produced the lowest, 0.20. It was found that the decolourisation of synthetic dyes by the catalyst was pH dependant. All catalysts performed well within the range pH 4-8. The Co- and Cu-containing catalysts were also active up to pH 12. $MnO{\cdot}Fe_2O_3$ performed well at pH 2 unlike the other catalysts. In all of the cases mentioned, 85% or greater decolourisation of dye was achieved. Finally, the stability of the catalysts was investigated and it was found that there was very little metal loss. There was no decrease in decolourisation efficiency after five 72 hour cycles. It was concluded that iron oxide (magnetite) and mixed iron oxides (Cu, Co and Mn ferrites) are effective catalysts for the oxidative decolourisation of dyes in the presence of hydrogen peroxide.

Tang et al. (2005) investigated the use of a novel catalyst for photo-assisted degradation of dyes. The catalyst was prepared by the immobilization of Fe (III) onto collagen fibre, which contains an abundance of –OH, -COOH and NH_2 functional groups. It was found that the Fe (III) reacted with –COOH in the formation of hydroxyl complexes. A typical acidic dye, Orange II (CI 11270) was used as the model pollutant for the catalytic activity experiments. Initial investigations indicated that the natural pH of Orange II was pH 6.2, which decreased to pH 3.7 after the degradation reaction. The complex of Fe (III) and –COOH of collagen was found to be stable in the range pH 3.2-

7.0. This allowed all experiments to be carried out at the natural pH of orange II solutions (pH 6.2) in order to prevent iron leaching during the process. Figure 1.23 displays the results for the degradation of Orange II. It can be seen that a fast degradation was achieved in the presence of H_2O_2 and UV. The fastest degradation was observed when using H_2O_2, UV and the catalyst. In this system, the degradation equilibrium of Orange II was reached in only 20 minutes. It can also be seen that H_2O_2 and the catalyst was able to contribute to the degradation of the dye without UV. After 20 minutes, 80% degradation was achieved.



(1) H_2O_2 (5mM) and UV (4W lamp), **(2)** H_2O_2 (5mM) and UV (8W lamp), **(3)** H_2O_2 (5mM), UV (4W lamp) and catalyst (2g), **(4)** H_2O_2 (5mM), UV (8W lamp) and catalyst (2g), **(5)** H_2O_2 (5mM) and catalyst (2g), **(6)** UV (8W lamp) only and **(7)** Reduction of dye due to adsorption by the catalyst (2g)

Figure 1.23 A Graph to illustrate the degradation of Orange II by various systems

As there was no obvious difference in the extent of degradation with or without the catalyst in the presence of H_2O_2 and UV at 60 minutes, TOC measurements were taken. The TOC residues for the two were around 93% with the catalyst and 50% without. This indicated that the degree of mineralization was enhanced with the use of the catalyst. It was found that after recycling ten times, Fe ions were leaching into solution during the process, which was investigated further using AAS. During the degradation

reaction, it was noticed that the amount of iron leaching first increases and then decreases as the reaction progresses. It was inferred that as Fe (III) was converted to Fe (II) the amount leaching increased. However, as Fe (II) was converted back to Fe (III) by the H_2O_2 in solution, the Fe (III) was able to re-bond with the collagen fibre. After these investigations, it was found that in total very small amounts of iron (0.25-0.80 mg/l) leached and this decreased as the degradation process progressed. The homogeneous contribution to catalysis was not reported in this study.

Degradation of phenol using Fenton Processes

Wastewater from chemical industries can contain high concentrations of phenol and its derivatives (KAVITHA and PALANIVELU, 2004). Such industries include; resin manufacturing, petrochemical, oil-refineries, paper making, coking and iron-smelting. Due to the high stability and solubility of phenol in water, much research has been focused on complete oxidation of organics to harmless products (CO_2 and H_2O). The main advantage of the Fenton's process in phenol decomposition is that reagents are safe to handle and environmentally benign.

Kavitha and Palanivelu (2004) compared different Fenton-related processes for the degradation of phenol. Table 1.11 summarises the results obtained for the level of phenol degradation in relation to the processes used.

Table 1.11 Degradation of phenol in relation to the Fenton process used

Process Used	Phenol Degradation	% Mineralization
UV/H_2O_2	1%	1%
Fenton	82%	41%
Solar-Fenton	95%	96%
UV-Fenton	99%	96%

[Phenol] = 2.12mM, pH = 3 ± 0.2, $[H_2O_2]$ = 30mM, $[Fe^{3+}]$ = 0.8mM and reaction time was 120mins.

Benzoquinone and aliphatic di and mono-carboxylic acids were identified as intermediate compounds formed during the reaction. Oxalic and acetic acids were also identified as major products of catalysis, both of which are resistant to Fenton reaction

resulting in a lower level of mineralization. The presence of such aliphatic acids suggests complete oxidation of aromatic structures followed by cleavage to aliphatic ones.

Lee et al. (2006) explored the use of Fenton-like treatment for the degradation of phenol by a heterogeneous catalyst (modified iron oxide). It had been suggested that the draw backs of the Fenton process was the acidic pH required and the ferric ions produced under Fenton treatment. These ions generate a significant amount of ferric hydroxide sludge which requires separation and disposal. The use of heterogeneous catalyst with H_2O_2 as an alternative has been suggested; however the decomposition rate is reported to be slower than the classic Fenton reaction at acidic pH. Lee et al. (2006) were concerned with the development of a new heterogeneous catalyst to increase the rate of decomposition of organic contaminants. Phenol was chosen as the probe compound in their study. The catalyst was prepared by dissolving a mixture of Fe (II) and Fe (III) in water followed by the addition of sodium hydroxide to adjust the pH to 9. The solution was stirred for 40 minutes, where a colour change from red to reddish brown was observed, where Fe (II) is converted to Fe (III) on calcination. The precipitate was filtered, washed with water and air-dried. Once dry, the products were placed in a furnace at 400, 600, 800 and 1000^{o}C for 2 hours. The temperature was then decreased to room temperature.

Lee et al. (2006) studied the degradation of phenol with different iron oxides and hydrogen peroxide. The conditions for the reactions were: pH 3, 400ppm hydrogen peroxide, 200ppm phenol and catalyst (0.1% Fe). From the results it was observed that the catalytic activity for phenol decomposition followed the sequence: Ferrous Iron > Synthesized Iron Oxide >> Magnetite > Hematite > Goethite. The respective phenol decompositions after 50 minutes are given below in Table 1.12. Modified iron oxide synthesized in the laboratory and calcined at 600^{o}C behaved in a similar way to that of the ferrous ion at pH 3.

Table 1.12 Catalytic activity of various heterogeneous catalysts towards phenol

Catalyst Used	Phenol Decomposition
Goethite (Fe (III))	10%
Hematite (Fe (III))	45%
Magnetite (Fe (II), Fe (III))	55%
Synthesized Iron Oxide calcined at 400^{o}C	45%
Synthesized Iron Oxide calcined at 600^{o}C	100%
Synthesized Iron Oxide calcined at 800^{o}C	35%
Synthesized Iron Oxide calcined at 1000^{o}C	20%
Ferrous iron	100%

The importance of pH on the reaction was also investigated over 5 minutes, which indicated that when using ferrous ion, the optimum pH was 3 giving 100% phenol decomposition. When investigating the synthesized iron oxide calcined at 600^{o}C, it was found that a pH range from 3 to 7 gave 100% phenol decomposition, above pH 7 attributed to 10% decomposition. Investigations using Atomic Absorption Spectroscopy were carried out throughout the reaction in order to determine the generation of soluble iron. The detection limit was 0.1ppm and no iron was detected throughout the reaction. The surface oxidation state of the iron oxide catalyst calcined at 600^{o}C was between +2 and +3 (ca. +2.8) measured by X-ray photoelectron spectrometer (XPS). The catalyst synthesized in the laboratory was less porous than Geothite as the mean diameters were similar, 50.7μm for the synthesized catalyst and 44-74μm for Geothite; however, the surface areas were found to be very different, 12.9m^2/g synthesized catalyst and 215m^2/g goethite. Lee et al. (2006) also found that the decomposition of H_2O_2 was consistent with the degradation of phenol.

Photo-Fenton catalysis has been discussed in detail for the degradation of phenol (NOORJAHAN et al.; 2005, MARTINEZ et al., 2005). Noorjahan et al. (2005) were involved with the preparation of a stable heterogeneous photo-Fenton catalyst based on zeolites (HY). Table 1.13 to Table 1.16 display the results when investigating the effect of phenol (50mls, 10^{-4}M) with known concentrations and volumes of H_2O_2.

Table 1.13 Comparison of Fenton conditions at pH 5.6 for the degradation of phenol

Catalysis Conditions	% Phenol Degradation
UV + Fe(III)-HY + H_2O_2	100% (60mins)
Homogeneous Photo-Fenton (with H_2O_2)	80% (180mins)
UV + Fe(III)-HY	30% (150mins)
Dark + Fe(III)-HY + H_2O_2	20% (150mins)
Photolysis	10% (150mins)

[Phenol] = 10^{-4}M, [H_2O_2] = 10^{-3}M and 25mg catalyst

Table 1.14 Effect of Fe (III) loading on the degradation of phenol (UV + Fe(III)-HY + H_2O_2)

Fe (III) loading	% Phenol Degradation (60mins)
5 wt% of catalyst	85%
2 wt% of catalyst	90%
1 wt% of catalyst	98%
0.5 wt% of catalyst	98%
0.25 wt% of catalyst	98%
0.125 wt% of catalyst	98%

[Phenol] = 10^{-4}M, [H_2O_2] = 10^{-3}M, pH = 6 and 25mg catalyst

Table 1.15 Effect of pH on the degradation of phenol (UV + Fe(III)-HY + H_2O_2)

pH	% Phenol Degradation
3	98% (60mins)
6	98% (60mins)
8	97% (180mins)

[Phenol] = 10^{-4}M, [H_2O_2] = 10^{-3}M and 25mg catalyst

Table 1.16 Effect of hydrogen peroxide on the degradation of phenol (UV + Fe(III)-HY + H_2O_2)

H_2O_2 Concentration	% Phenol Degradation
10^{-3}M	98% (60mins)
10^{-2}M	90% (180mins)
5 x 10^{-4}M	90% (180mins)

[Phenol] = 10^{-4}M, pH = 6 and 25mg catalyst

In all cases, the solutions were evaluated for Fe (II) ions leaching from the heterogeneous catalyst by AAS. It was found that with the highest loading of iron (5 wt% of catalyst), the amount of iron detected was less than 2% of the total iron on the catalyst. When the catalyst was reused without calcination, there were slight differences in the degradation rate; however the completion time of the reaction was almost the same. The catalyst was also reused after calcination causing the degradation rate to be restored.

Martínez et al. (2005) studied the use of a novel Fe-containing SBA-15, for heterogeneous photo-Fenton degradation of phenol containing solutions. SBA-15 is a material of silica nanoparticles with larger pores of 4.6 to 30 nanometers. The iron-containing SBA-15 meso-structured material was prepared by co-condensation of iron (III) and silica under acidic conditions. Promotion of the precipitation of crystalline iron oxide particles was achieved by ageing of the solution at 110^{o}C for 24 hours at pH 3.5. After ageing, the solid product was recovered by filtration and air dried at room temperature overnight. The influence of loading and H_2O_2 concentration were investigated and the results provided in Table 1.17.

Table 1.17 The effect of iron-loading and H_2O_2 concentration on the degradation of phenol

Fe (g catalyst per litre solution)	$[H_2O_2]$ ppm	% Aromatic Removal	% H_2O_2 conversion
0.5 g/l	800	80	68
	2450	95	65
	4111	90	55
1.5 g/l	800	94	100
	2450	93	85
	4111	95	68

$[TOC]_0$ = 380ppm and pH = 5.5

In all cases it was found that less than 6% iron leached from the catalyst after 240 minutes of reaction. The highest level of iron leaching obtained was 5.2% (11.5 ppm) when using 1 g/l catalyst and 2450 ppm hydrogen peroxide. In all cases the levels of Fe found in solution when using 1 g/l loading were greater than those detected for 0.5 and 1.5 g/l loadings, hence why experimental data was not given for this sample. Finally

absorption experiments were carried out which indicated negligible contribution to degradation (5%).

1.4 Wet Oxidation of Phenol

There is a lot of information available in literature relating to the wet oxidation of phenol (Santos et al., 2002, Santos et al., 2005, Tryba et al., 2006, Bremner et al., 2006). In all cases the reaction pathways illustrated in Figure 1.24 have been identified as possible routes of phenol decomposition. Santos et al. (2002 and 2005) identified and quantified phenol and organic intermediates by HPLC. They used a Nucleosil C-18 5μm column (250mm by 4.6mm) and 4mM sulphuric aqueous solution as the mobile phase. Flow rate was 1 to 1.9 ml min^{-1} and the UV detector was used at wavelengths 192, 210, and 244nm. To assist with their investigation, both Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) values were measured. In order to determine the presence of quinines, 2,4-dinitrophenylhydrazone was precipitated in the effluents (50mls) being evaluated by an acidifying solution (10ml, H_2SO_4 50mM) of 2,4-dinitrophenylhydrazine (25mM) in ethanol.

Tryba et al. (2006) investigated the time trend of phenol and the generation of ring-retaining products such as benzoquinone (BQ), hydroquinone (HQ) and catechol by HPLC. Concentrations of phenol were determined at the wavelength 269nm and BQ and HQ at 246 and 289nm respectively. It has been suggested that the conversion of phenol to catechol is likely to be more advantageous for complete mineralization of phenol which is supported by the reaction pathways given above. This was again supported in the research carried out by Bremner et al. (2006). Phenol and reaction intermediates were determined again by HPLC with UV detector at 246nm. The mobile phase was a mixture of water / 85% phosphoric acid (99/1 $^{v}/_{v}$) at a flow of 1 ml min^{-1}.

The products of phenol decomposition using the wool catalyst in the presence of hydrogen peroxide can initially be determined in the same manner. This can be done by extracting samples during static cycles of catalysis followed by HPLC analysis adopting the conditions mentioned above. Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) measurements throughout catalysis would provide an indication of the

degree of mineralisation. The Themalox Total Inorganic Carbon/Total Carbon (TIC/TC) measurement instrument is available at the University. Total carbon (TC) measurements can be obtained by heating the solution of interest in an oven (680^{o}C) over a platinum catalyst with oxygen present. Carbon dioxide is then measured using an infra-red detector. TIC can be obtained in a similar fashion, the solution is heated without a catalyst at 120^{o}C with oxygen and the resultant carbon dioxide measured as before. TOC can be calculated by subtracting the TIC from the TC.

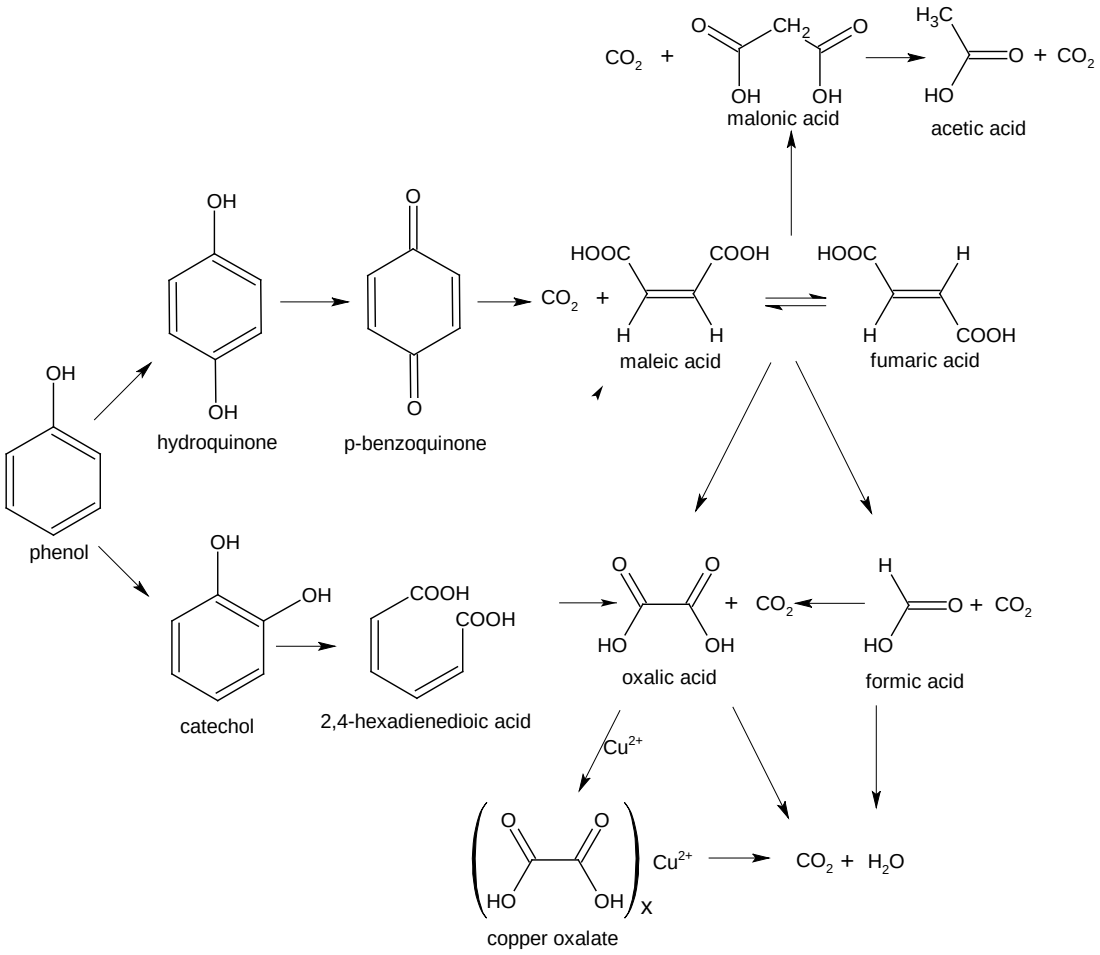


Figure 1.24 Possible Reaction Pathways for the Wet Oxidation of Phenol (SANTOS et al., 2005)

This work is devoted to adding value to low value wool by the development of a solid phase oxidation catalyst supported on wool for the treatment of industrial wastewater. It is recognised that homogeneous systems have distinct disadvantages. They introduce metal cation pollutants into sewage, are not easy to replace, cannot be regenerated or used catalytically. As yet very few attempts have been made to develop a heterogeneous oxidation catalyst based on the hydrogen peroxide / Iron (III) system, and no attempts have been made using wool fibre as support. The few solid phase catalysts reported in the literature act by leaching iron (II) or (III) from the catalyst, whereupon catalysis takes place in the homogeneous phase (BELTRAN et al., 2005). Immobilisation of a metal cation on wool fibre whilst still remaining catalytically active towards the decomposition of organic molecules in the absence of UV light is not trivial. It is crucially dependant on the nature of the immobilisation.

Chapter 2 Catalyst Production

2.1 Introduction

There were three main aims for this initial stage of catalyst development. These are outlined below:

1. Comparison of wool scouring methods,
2. Chemical modification of wool using hydrazine and hydroxylamine followed by optimisation,
3. Impregnation with aqueous solution of Fe (III) salt to produce an oxidation catalyst.

2.1.1 Scouring of wool

Wool scouring is a washing process that all wool undergoes prior to further treatment/processing. There are two types of scouring currently in operation, being the traditional water based scour with detergent and the solvent based scour. In both cases the systems are designed to remove the suint, dirt and dust from the wool to produce a clean product ready for further processing.

The purpose of this experiment was to evaluate two methods for scouring of wool with regards to their iron (III) uptake post degreasing. Three variations of wool were used:

1. Industrially scoured top wool (WOOLMARK);
2. Raw greasy DEFRA top wool (provided by CSL);
3. Raw, very dirty and greasy DEFRA wool (provided by CSL);

The two scouring systems evaluated were:

1. Shake-flask solvent degreasing.
2. Non-ionic scouring without alkali treatment.

Results from these experiments would indicate the best degreasing method and wool type to use in maximizing the iron (III) uptake for future investigations.

2.1.2 Wool modification followed by impregnation with Fe (III) Salts

Previous work in the modification of PAN fibre highlighted the benefits of modification with hydrazine and hydroxylamine salts. It suggested that improved iron (III) uptake could be achieved along with promoting catalytically active iron (III). Another advantage of modification highlighted in the papers was the improved fixation of iron to the fibres.

It was expected that iron uptake would be poor without modification of wool. The various chemical reactions of wool were discussed previously in section 1.2.2. Modification using the regimes investigated in the previous work on PAN was expected to improve the iron uptake, fixation and catalytic activity of the wool catalyst. The purpose of this experiment was to evaluate the effects that chemical modification of wool has on iron uptake. Three modifications were investigated as an initial study. These were:

1. Hydrazine Modification
2. Hydroxylamine Modification
3. 50:50 Mixture (50% Hydrazine and 50% Hydroxylamine) Modification

A second part of the study was to investigate the effects of elevated impregnation temperatures on iron uptake, distribution and fixation. This was only performed on hydrazine modified wool.

2.2 Materials and Chemicals

Wool fibre:

Industrially scoured wool from Woolmark (white fibres), DEFRA raw wool (white fibres) from Central Science Laboratory, York, now known as FERA (The Food and Environment Research Agency), raw Dark Grey Herdwick (grey and black fibres), raw Swaledale (white and black fibres), raw Halfbreds (white fibres), raw Blackface (white fibres) and raw Crossbreds (white fibres) along with corresponding industrially scoured samples supplied by Thomas Chadwick and Sons, Dewsbury, UK.

Scouring:

Non-ionic surfactant, UPL (Drummond Parkland)

Ethanol (Aldrich)

Modification & Impregnation:

Hydrazine dihydrochloride (Aldrich)

Hydroxylamine monohydrochloride (Aldrich)

Sodium hydroxide (Aldrich)

Ferric chloride hexahydrate (Aldrich)

2.3 Methods

2.3.1 Scouring by solvent

All three types of wool were subjected to the following procedure. Wool (2g) was placed in a sealed flask containing an ethanol-water solution (60% and 40% respectively, 100ml). The flask was mechanically shaken in a heated water bath (60^{o}C, 30 minutes). The wool was washed with distilled water, dried and air conditioned.

2.3.2 Non-ionic scouring

All three types of wool were subjected to the following procedures. The scouring was performed in three stages.

Stage 1:

Wool (2g) was treated with distilled water (200ml, 10 minutes at 60^{o}C). Any excess water was wrung out after treatment.

Stage 2:

The wool from stage 1 was treated in the presence of non-ionic, UPL surfactant (2g/l). This took place in water medium (15 minutes at 60^{o}C). Excess solution was again wrung out.

Stage 3:

Wool from stage 2 was treated in the presence of UPL surfactant (1g/l). This again took place in water medium (15 minutes at 60^{o}C). After treatment, excess solution was run off. The wool was washed with distilled water, dried and air conditioned.

In all stages the liquor to wool ratio (ml:g) was 100:1. All treatments were carried out in a continuous mechanical shaking bath.

2.3.3 Modification

Three separate samples of non-ionic scoured wool were weighed in preparation for chemical modification (3.1g). Each sample was suspended in its respective modification solution, as identified from the previous work with PAN (Ishtchenko et al., 2003b and 2003c). The solutions were as follows:

1. Hydrazine Solution: 200ml containing 30g/l of hydrazine dihydrochloride;
2. Hydroxylamine Solution: 200ml containing 42g/l of hydroxylamine monohydrochloride;
3. 50:50 mixture: 100ml of 30g/l hydrazine dihydrochloride and 100ml of 42g/l hydroxylamine monohydrochloride.

Each modification solution had undergone a pH adjustment (either pH 9.5 or 7) with sodium hydroxide pellets. The wool samples were then left in solution and heated (100-101^{o}C) for 2 hours. Refer to diagram in Figure 2.1 for apparatus setup.

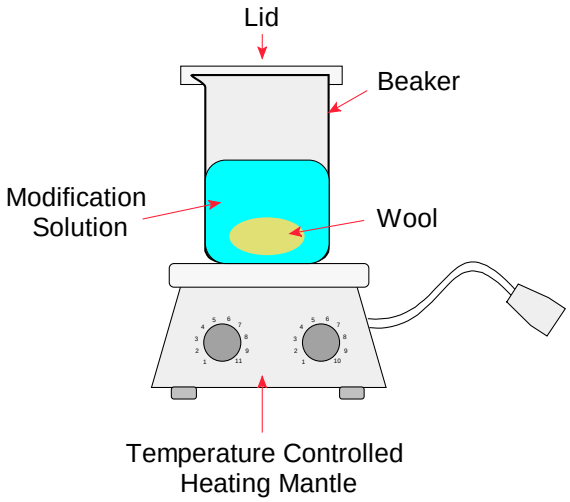


Figure 2.1 Apparatus for the Modification Process

On completion of the modification process each sample was washed thoroughly with double distilled water (approximately 3 litres). The samples were then left to dry under controlled conditions (24 hours). After drying, each sample was impregnated in the same way as previously described below.

2.3.4 Wool impregnation with Fe (III) salts

Unmodified wool (1g) was placed in a sealed vial containing ferric chloride in solution (0.1M Fe^{3+} solution, 50ml at pH = 1.7). The sealed vial was attached to a rotator for continuous shaking (room temperature for 24 hours). All three types of unmodified wool from both degreasing methods were subjected to this procedure resulting in six samples. Once complete, the wool was removed from the solution and thoroughly washed with double distilled water.

2.3.4.1 Impregnation at elevated temperature

The original parameters of impregnation described above were essentially kept constant. Hydrazine modified wool was subjected to an impregnation at an elevated temperature

(60°C) using a reflux system. A re-circulating condenser was used as the system was to be left unattended overnight. The system assembly is illustrated in Figure 2.2.

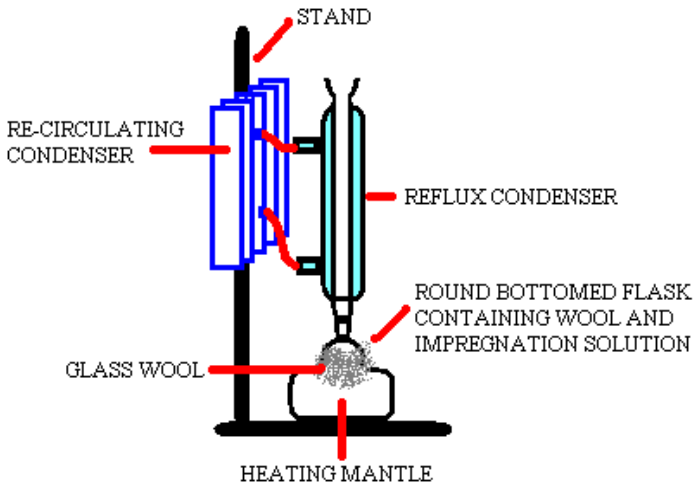


Figure 2.2 Apparatus for Impregnation at Elevated Temperatures

2.3.5 Determination of total Iron on wool and in solution by Atomic Absorption Spectroscopy

Calibration Method:

Standard solutions (1, 2, 3, 4 and 5ppm) of Fe^{3+} were prepared and analysed using Atomic Absorption Spectroscopy (AAS) to produce a calibration graph with respect to concentration. Each solution was analysed in triplicate. AAS is only linear up to 5ppm.

Total iron determination for each wool sample:

Impregnated wool (0.1g) containing Fe^{3+} cations was weighed out and then heated in hydrochloric acid (2M, 25ml) to dissolve all iron from the fibres. The solution was filtered and the fibres washed with double distilled water. The filtrate and washings were collected and placed in a volumetric flask (50ml) and double distilled water was used to dilute the solution up to the mark. The samples were then analysed in triplicate using AAS. This process was carried out twice for each sample and results averaged.

The total Fe content in the solution phase after both wool-EDTA fixation studies (see Section 2.3.6) and catalytic studies were directly analysed for Fe by AAS technique.

2.3.6 Fixation of Fe (III) to wool

The main purpose of this experiment was to evaluate how well Fe^{3+} ions are fixed to the wool fibres as it would be undesirable for ions to leach from the fibres. This can be evaluated using a strong complexing agent, such as, disodium-EDTA. It works by complexing with Fe^{3+} ions at pH 5 (Vogel 1989) and results in their removal from the wool into solution if they are not strongly fixed. Wool fibres (0.1g) containing the metal cation were thoroughly ground and left in contact with disodium-EDTA (0.5M, $5cm^3$) for 24 hours.

An aliquot of the wool-EDTA solution (1ml) was diluted with distilled water and made up to the mark in a volumetric flask (50ml). The total iron content of the solution was determined directly by AAS as described above. Each sample was analysed in triplicate. Two replicates for each sample were performed.

2.4 Results and Discussion

2.4.1 Scouring Study

Three different types of wool fibres were scoured by two scouring systems, solvent degreasing (60% Ethanol ($^{v}/_{v}$)) and non-ionic surfactant scouring. Table 2.1 and Table 2.2 show the results of wool scouring, weight loss and iron uptake.

Table 2.1 Results from the degreasing study for both shake-flask solvent degreasing and scouring

Wool	**Clean Top Wool (WOOLMARK)**		**Greasy DEFRA Top Wool**		**Dirty & Greasy DEFRA Wool**	
Degreasing Method	Solvent	Scouring	Solvent	Scouring	Solvent	Scouring
Weight Before	2.0000g	2.0000g	2.0000g	2.0000g	2.0000g	2.0000g
Weight After	1.8565g	1.8794g	1.5235g	1.4714g	1.5094g	1.3494g
% Weight Loss	7.18%	6.03%	23.83%	26.43%	24.53%	32.53%
Touch/Visual Comments	Not Greasy	Not Greasy	Still greasy	Not Greasy	Still greasy and dirt present	Not Greasy but dirt present

It is evident that the wools with less processing (as provided by CSL) have a greater weight loss after scouring. This is due to the removal of grease, waxy lipids and dirt. The Woolmark wool had already been scoured prior to treatment at the University. Thus, less dirt and grease was present to be removed. Raw wool fleeces usually contain less than 65% clean fibre. Before treatment they can contain wool wax, skin flakes, suint, sand, dirt and vegetable matter.

Table 2.2 Impregnation results for wools degreased with both solvent and scouring methods

Wool	Degreasing Method	Iron Uptake (mmol/g wool)	Physical appearance of wool post impregnation
Clean Top Wool (WOOLMARK)	Solvent	0.0348	Brown colouration of outer fibres. Wool became compacted/ clumped together. The impregnation was not uniformly distributed.
	Scouring	0.0606	Uneven distribution of brown colouring across the bundle of fibres. Wool became compacted/ clumped together.
Greasy Top Wool (DEFRA)	Solvent	0.0436	The impregnation appeared to be slightly more uniform than for WOOLMARK samples. It was noticed that the shade of brown was lighter and no compacting occurred.
	Scouring	0.1180	Slight variation of dark brown observed across the fibre bundle. Wool did not compact and was similar to the WOOLMARK scoured sample.
Dirty & Greasy Belly Wool (DEFRA)	Solvent	0.0667	The intensity of brown colouring was greater than WOOLMARK samples. Colour distribution was quite uniform with no compacting.
	Scouring	0.0498	This sample did not compact. However, the intensity of colour was less than any other sample evaluated.

The wools provided by DEFRA were coarse whereas the WOOLMARK top wool was very fine. This may be why the clean-top wool (WOOLMARK) compacted and became very difficult to handle on impregnation. In general, the results indicated that a deeper colour, suggesting a higher iron uptake, could be achieved by using the non-ionic scouring method. Solvent/water degreasing was unable to eliminate the grease, which

probably prevented iron uptake. It was found that the DEFRA sample by non-ionic scouring had the highest iron uptake.

The presence of alkali in scouring solution is optional because there would seem to be sufficient removal of fatty compounds e.g. acids and waxes from the wool surface, without using alkali (confirmed by SEM, results presented in Section 4.4.2.1). Moreover, for our study alkali was not desirable, as it could slightly modify the surface of the wool during the scouring procedure adversely changing the nature of the chemical groups resulting in a less successful modification of these groups with the modifying agents, hydrazine and hydroxylamine. Additionally, not incorporating alkali in the scouring step will also result in a reduction of the cost of the process.

2.4.2 Modification

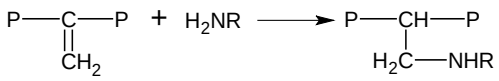
Wool fibre was modified and impregnated with 0.1M $FeCl_3$ at pH 1.7 as described previously in Section 2.1.2. Keeping the pH of the iron (III) solution below 2 was important, as this prevents the precipitation of oxo-/hydroxo iron species on the wool. Results of the study are presented in Table 2.3.

Table 2.3 Visual observations on modification (pH 9.5) and Fe (III) impregnation of DEFRA top wool

Sample ID	Comments
Impregnated scoured & hydrazine modified wool (Room Temperature).	Distribution of colour appeared uniform throughout the wool bundle. Fibres did not compact and the colour was a more intense shade of orange/brown than observed for unmodified wool.
Impregnated scoured & hydrazine modified wool (60^oC).	This appeared similar to the sample impregnated at room temperature. The shade of orange/brown was slightly lighter.
Impregnated scoured wool (Room Temperature).	The wool collapsed post impregnation. There was an uneven distribution of colouring throughout the wool bundle.
Impregnated scoured wool (60^oC).	The wool bundle appeared to have a uniformly distributed colour of orange. Unlike the other samples, the wool appeared to swell.

It was noticed from Table 2.3 that for modified wools, regardless of temperature, the colour distribution on impregnation appeared uniform. On comparing the modified wools with unmodified wools impregnated at room temperature, it was found that the colour changes were more noticeable. All of the wools evaluated showed an orange/brown colour to be present across the fibre bundle. In each case the wools changed from a beige/white colour to an orange/brown shade.

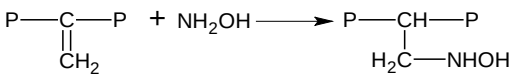
Both hydrazine sulphate and hydroxylamine have been used as dye bath additives (SIMPSON, 1996). Hydroxylamine was found to be superior when reducing the yellowness of wool fibres (SIMPSON, 1999). Dye bath additives are known for their ability to bind with reactive and unstable chemical groups in wool, thus preventing dye bath yellowing. The causes of wool yellowing are varied and no single remedy is likely to give total success (SIMPSON, 1997a). Reaction with alkylamine under alkaline conditions showed that cystine was vulnerable to cleavage of the disulphide bond (SIMPSON, 1997b). Dehydroalanine, a product of this breakdown was able to further react with alkylamines as shown in Figure 2.3.



(P = Protein Chain)

Figure 2.3 Reaction of Dehydroalanine with Alkylamines

The same mechanism with hydroxylamine would result in a pendant hydroxamic acid group $–CH_2$-NH-OH as given in Figure 2.4 (SIMPSON, 1997a). After treatment of wool with hydroxylamine liquors tested with $FeCl_3$ in acid solution produce a characteristic ruby red colour formed by the acid complex, a hydroxamic complex of Fe^{3+}.



(P = Protein Chain)

Figure 2.4 Suggested Mechanism for the Reaction of Dehydroalanine with Hydroxylamine

Results for total Fe uptake by WOOLMARK and DEFRA top wool modified at pH 9.5 and 7 are presented in Table 2.4 and Table 2.5.

Table 2.4 Iron Uptake Results on WOOLMARK and DEFRA top wool modified at pH 9.5

Sample ID	Sample description	Mass of the wool for AA-AES, g	Absorbance readings	[Fe], ppm	$[Fe]_{average}$, mmol/g wool	[Fe] Removed by EDTA, %
	WOOLMARK top wool [a]					
1	Scoured, modified wool with hydrazine only and impregnated with Fe(III) at RT	0.0547 0.0577	0.015 0.017	0.741 0.899	0.013	0.001
2	Scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at RT	0.0589 0.0609	0.032 0.039	1.848 2.291	0.031	0.000
3	Scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at RT	0.0559 0.0575	0.024 0.024	1.342 1.342	0.021	0.000
4	Scoured, non-modified wool, impregnated with Fe(III) at RT	0.0604 0.0632	0.010 0.011	0.456 0.519	0.007	0.010
5	Industrially scoured, non-modified wool, impregnated with Fe(III) at RT	0.0586 0.0576	0.027 0.028	1.532 1.595	0.024	0.008
6	Industrially scoured, non-modified wool (no Fe impregnation)	0.1519 0.1521	0.030 0.030	0.083 0.083	0.0005	N/A
7	Scoured, non-modified wool (no Fe impregnation)	0.1141 0.1364	0.000 0.000	0.000 0.000	0.000	N/A
	DEFRA top wool [b]					
8	Laboratory scoured, modified wool with hydrazine only and impregnated with Fe(III) at RT	0.1000 0.1000	0.192 0.193	4.911 4.936	0.088	0.002
9	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at RT	0.0308 0.0288	0.42 0.39	2.060 1.960	0.060	0.000
10	Laboratory scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at RT	0.0309 0.0306	0.59 0.59	3.030 2.980	0.088	0.001
11	Laboratory scoured, modified wool with hydrazine only and impregnated with Fe(III) at 60^0C	0.1000 0.1000	0.136 0.146	3.487 3.743	0.065	0.000
12	Laboratory scoured, non-modified wool impregnated with Fe(III) at 60^0C	0.1000 0.1000	0.2238 0.2242	5.724 5.734	0.103	0.011

Term 'scoured' refer to the Woolmark top wool subjected to both industrial and laboratory scouring:

(a) equations used for Fe (ppm) determination were y(abs) = 0.0158 x (conc) + 0.0028 (samples 1-5) and y(abs) = 0.1551·x(conc) + 0.0171 (samples 6 and 7); volume of solution for AA-AES analysis was 50mL;

(b) equations used for Fe (ppm) determination were y(abs) = 0.0391·x(conc) + 0.0000 (samples 8, 11 and 12); y(abs) = 0.186·x(conc) + 0.026 (samples 9 and 10).

Comparing three types of modifications at pH 9.5 (hydrazine, hydroxylamine and 50:50 hydrazine/hydroxylamine mixture), it can be seen from the results in Table 2.4, that the highest Fe(III) uptake can be obtained for the hydrazine modified DEFRA top wool (sample 8).

There is very little or no iron found on the industrially (sample 6) or laboratory (sample 7) scoured WOOLMARK top wools. Surprisingly, increasing the temperature of modification up to 60^{o}C results in a lower Fe (III) uptake as shown by the hydrazine modified wool (samples 8 and 11). Additionally, both hydrazine samples (room temperature and 60^{o}C) were evaluated for iron fixation using Na_2-EDTA. Analysis showed there to be no iron removed (0% iron desorption from the wool) by the Na_2-EDTA complexing agent, indicating that the iron was fixed strongly to the wool fibre. For all samples evaluated for fixation the results were pleasing indicating that less than 1% of the iron was removed from wool.

Comparing the two types of wool, WOOLMARK and DEFRA, it can be seen that Fe (III) uptake is higher on the DEFRA than the WOOLMARK top wool. It was noticed, that modification of the wool fibre at pH 9.5 caused significant destruction to the fibres. It was decided to perform modification of wool at lower pH, such as neutral pH 7, to see whether any improvement in physical appearance of wool took place. It was found that modification at the lower pH did result in a less friable fibre. The iron uptake results for wools modified at pH 7 are displayed in Table 2.5.

Table 2.5 Iron uptake on WOOLMARK, DEFRA top wools and Thomas Chadwick wools modified at pH 7

Sample ID	Sample description	Mass of the wool for AA-AES, g	Absorbance readings	[Fe], ppm	$[Fe]_{average}$, mmol/g wool	[Fe] Removed by EDTA, %
	Woolmark top wool [a]					
13	Scoured, modified wool with hydrazine only and impregnated with Fe(III) at r.t.	0.0570 0.0586	0.012 0.010	0.582 0.456	0.008	0.001
14	Scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0597 0.0596	0.083 0.082	5.076 5.013	0.076	0.000
15	Scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at r.t.	0.0548 0.0606	0.044 0.051	2.608 3.051	0.044	0.002
16	Scoured, modified wool with hydrazine only (no impregnation with Fe(III))	0.1034 0.1032	0.00 0.00	0.000 0.000	0.000	N/A
17	Scoured, modified wool with hydroxylamine only (no impregnation with Fe(III))	0.1174 0.1104	0.00 0.00	0.000 0.000	0.000	N/A
18	Scoured, modified wool with 50:50 hydrazine/hydroxylamine (no impregnation with Fe(III))	0.0977 0.0920	0.00 0.00	0.000 0.000	0.000	N/A
	DEFRA top wool [b]					
19	Laboratory scoured, modified wool with hydrazine only and impregnated with Fe(III) at r.t.	0.0500 0.0507	0.08 0.10	0.311 0.444	0.007	0.001
20	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0451 0.0446	0.60 0.62	3.750 3.890	0.076	0.000
21	Laboratory scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at r.t.	0.0546 0.0515	0.36 0.36	2.166 2.166	0.037	0.001
22	Laboratory scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.0814 0.0812	0.14 0.15	0.660 0.730	0.007	0.011
23	Non – scoured (raw), non-modified wool, impregnated with Fe(III) at r.t.	0.0795 0.0769	0.10 0.21	0.444 1.172	0.009	0.102
24	Non-scoured, non-modified wool (no Fe(III) impregnation)	0.2066 0.2433	0.28 0.22	1.627 1.227	0.006	N/A
25	Laboratory scoured, non-modified wool (no Fe(III) impregnation)	0.1189 0.1290	0.00 0.00	0.000 0.000	0.000	N/A
	Herdwick wool [c]					
26	Mill scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.1100 0.0800	0.107 0.080	1.334 1.000	0.055	0.000
27	Mill scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at r.t.	0.0700 0.1200	0.050 0.087	0.625 1.083	0.040	0.002
28	Mill scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.1000 0.1300	0.030 0.043	0.375 0.542	0.020	0.101
29	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0833 0.1002	0.09 0.08	1.636 1.455	0.076	0.000
30	Laboratory scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at r.t.	0.0829 0.1182	0.06 0.09	1.091 1.576	0.059	0.001

Sample ID	Sample description	Mass of the wool for AA-AES, g	Absorbance readings	[Fe], ppm	$[Fe]_{average}$, mmol/g wool	[Fe] Removed by EDTA, %
31	Laboratory scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.1030 0.0867	0.06 0.25	1.091 4.545	0.047	0.102
32	Non-scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.0800 0.0900	0.057 0.050	0.708 0.625	0.036	0.110
	Swaledale wool [d]					
33	Mill scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.1050 0.1020	0.156 0.119	7.378 6.780	0.107	0.000
34	Mill scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe(III) at r.t.	0.1010 0.0920	0.115 0.186	6.572 5.321	0.055	0.001
35	Mill scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.0900 0.0940	0.086 0.084	2.448 2.390	0.024	0.101
36	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0920 0.0990	0.137 0.140	3.905 4.010	0.074	0.000
37	Laboratory scoured, modified wool with 50:50 hydrazine/hydroxylamine and impregnated with Fe (III) at r.t.	0.0980 0.0990	0.043 0.043	10.805 10.805	0.098	0.002
38	Laboratory scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.0920 0.1020	0.053 0.070	1.505 2.000	0.016	0.110
39	Non-scoured, non-modified wool, impregnated with Fe(III) at r.t.	0.0950 0.0900	0.131 0.089	3.733 2.533	0.030	0.100
	Crossbred wool [e]					
40	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0970 0.0830	0.027 0.022	4.271 3.438	0.077	0.000
41	Mill scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0980 0.0840	0.025 0.023	3.958 3.542	0.074	0.000
	Halfbreds wool [f]					
42	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0940 0.0930	0.020 0.020	3.177 3.125	0.060	0.000
	Blackface wool [g]					
43	Laboratory scoured, modified wool with hydroxylamine only and impregnated with Fe(III) at r.t.	0.0840 0.0800	0.030 0.029	4.740 4.531	0.101	0.002

Woolmark top wool was both industrially and laboratory scoured;
(a) equations used for Fe (ppm) determination were **y(abs) = 0.0158·x(conc) + 0.0028** (samples 13-15) **and y(abs) = 0.1551·x(conc) + 0.0171** (samples 16-18)
(b) equations used for Fe (ppm) determination were **y(abs) = 0.151·x(conc) + 0.033** (samples 19-23) and **y(abs) = 0.15·x(conc) + 0.036** (samples 24 and 25)**;** volume of solution for AA-AES analysis was 50mL;
(c) equations used for Fe (ppm) determination were **y(abs) = 0.0799·x(conc) + 0.0000** (samples 26-29) **and y(abs) = 0.055·x(conc) + 0.0000** (samples 30-32)
(d) equation used for Fe (ppm) determination was **y(abs) = 0.035·x(conc) + 0.000** (samples 33-39)
(e) equations used for Fe (ppm) determination were **y(abs) = 0.0064·x(conc) + 0.0000** (sample 40) and **y(abs) = 0.0071·x(conc) + 0.0000** (sample 41)
(f) equation used for Fe (ppm) determination was **y(abs) = 0.0064·x(conc) + 0.0000** (sample 42)
(g) equation used for Fe (ppm) determination was **y(abs) = 0.0064·x(conc) + 0.0000** (sample 43)

At pH 7 as can be seen from the results of Table 2.5, the highest Fe (III) uptake is observed for hydroxylamine modified and the lowest for hydrazine modified wool, independent of the type of wool. Similar amounts of Fe (III) uptake were observed for each of the three modification regimes independent of wool type. It can be seen that non-scoured wools can produce high [Fe] content as observed for sample 24 (1.627 and 1.227 ppm). This can be attributed to the suint, dirt and vegetable matter that has not been removed from the sample prior to treatment.

Generally, laboratory scouring of Herdwick wool results in a slightly better uptake of Fe (III) than the mill scoured Herdwick wool samples, which could be due to a more efficient removal of the waxy top layer using laboratory scouring.

After Fe (III) impregnation there is only a negligible amount of Fe (III) found on the raw DEFRA top wool (sample 23) presumably because the greasy top layer prevented access of Fe (III) to the functional groups on the wool. The raw Herdwick and Swaledale wools had a larger than expected uptake of Fe (III) in comparison to that for the DEFRA wool, which was thought to arise from contamination with debris.

WOOLMARK and DEFRA top wool control samples (samples 16-18, 25) do not contain implicit Fe (III) in the fibres. A small amount of Fe (III) is present on the raw DEFRA top wool (sample 24) which could be due to dirt impurities on the wool which are removed after scouring.

Little difference in mechanical friability at pH 7 was observed between non-modified and modified wools, except the fact, that after modification with hydroxylamine and 50:50 hydrazine/hydroxylamine wool surface was more expanded (fluffed up). This might be an advantage for the wool catalyst because of the higher surface area.

It is evident from the results that modification regardless of wool type increases iron fixation. In general modified and impregnated wools exposed to Na_2-EDTA for 24 hours resulted in between 0 & 2% removal of iron. This increased to 10-12% for unmodified and impregnated wools.

Hydroxylamine modified wools can take up more Fe(III) from solution. This is likely to be attributed to the pendent hydroxamic acid group formed after modification with hydroxylamine, which is supported in a study by W S Simpson (1997b). He evaluated wool samples treated at pH 5, 7, and 9 with and without hydroxylamine at 100^{o}C for one hour. The wool samples were well rinsed and immersed in acidic $FeCl_3$. Samples pre-treated with hydroxylamine developed the characteristic ruby red colour, whereas other samples yielded a negative result (SIMPSON, 1997b). Samples of asparagine and glutamine were heated in hydroxylamine for 6 hours at pH 5, 7, and 9. After cooling the pH was adjusted to be acidic and $FeCl_3$ test solution added. The results for asparagine mirrored the observations made for wool. By comparison, the glutamine solutions gave a weakly positive result (SIMPSON, 1997b). When considering these experiments as a whole it seems likely that hydroxylamine reacts with amide and predominantly asparaginyl residues in wool to form hydroxamic acid side chains (Figure 2.5). It was found that the reaction was favoured by acidic or alkaline conditions rather than at neutral pH (SIMPSON, 1997b).

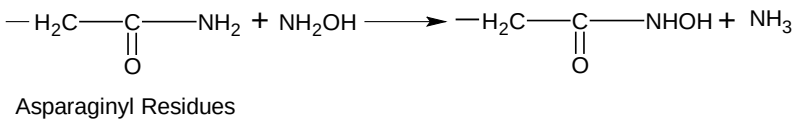


Figure 2.5 Proposed mechanism for the Reaction of Asparaginyl Residues with Hydroxylamine Modified Wool

This reaction mechanism supports that identified by Sidgwick (1910) who discussed in detail hydroxamic acids and the formation of (Figure 2.6). It was found that hydroxamic acids could be formed (even at low temperatures) by the action of hydroxylamine on amides, where ammonia was expelled.

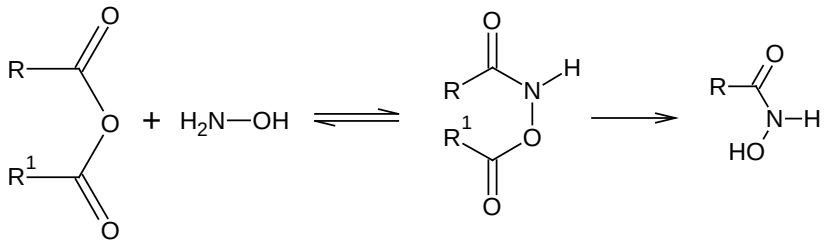


Figure 2.6 Reaction of Hydroxylamine to form Hydroxamic acid

A second possibility during modification with hydroxylamine is the formation of Oxime (Figure 2.7).

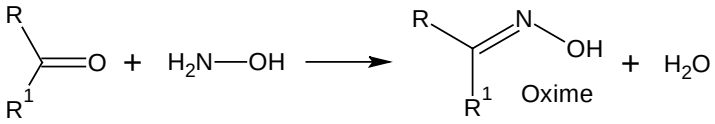


Figure 2.7 Reaction of Hydroxylamine to form Oxime

The reaction is quite general the oxime is formed by the action of hydroxylamine on a compound containing a carbonyl during heating (SIDGWICK, 1910). The rate of formation is greatest at around pH 4.7 and hardly detectable above pH 5. Hydrolysis is greatest at pH 2.3.

Finally, Day and Whiting (1970) discussed the formation of acetone hydrazone. Taking into account their findings, on treatment with hydrazine it is reasonable to suggest that hydrazones are formed (Figure 2.8). It is possible to hydrolyse hydrazone back to the carbonyl.

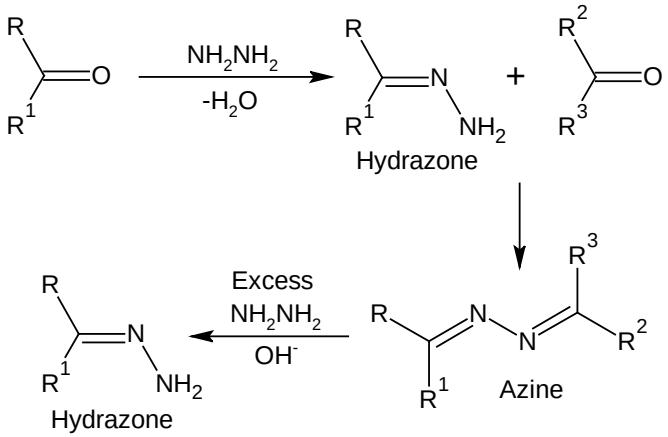


Figure 2.8 Formation of Hydrazone on treatment with Hydrazine

When considering the reactions presented for hydroxylamine in Figure 2.5 to Figure 2.7, it is probable that the major reaction is the formation of hydroxamic acid as the formation of oximes is unlikely. Modification takes place at pH 9.5 and 7, suggesting the formation of oximes is unlikely as they are hardly detectable above pH 5 as mentioned above. It is known that hydrazine promotes cross-linking. On formation of the azine during the reaction in Figure 2.8, it is possible that cross-linking may occur here.

2.5 Conclusions

In general when using the non-ionic scouring method, the results indicated a deeper colour post impregnation, suggesting a higher iron uptake. Solvent/water degreasing was unable to eliminate the grease, which probably prevented iron uptake.

It was noticed, that modification of the wool fibre at pH 9.5 caused significant destruction to the fibres. Fibres became fragile post modification especially WOOLMARK fibres which was easily observed in the general appearance and feel of the fibres. This destruction of the fibres was not unexpected due to the nature of wool when exposed to alkaline pH. It was found that a less friable fibre was achieved when modifying at pH 7 affording uptakes of 0.08 to 0.101 mmol/g wool for laboratory scoured, modified and impregnated fibres. At pH 7 the highest Fe (III) uptake was observed for hydroxylamine modified and the lowest for hydrazine modified wools, independent of the type of wool. Similar amounts of Fe (III) uptake were observed for each of the three modification regimes independent of wool type. When modification is carried out at pH 7 it was found that little or no iron was removed from the wool when exposed to Na_2-EDTA for 24 hours regardless of wool type. This result suggests that the iron is more strongly fixed to the wool with modification; however it is not known at this point whether the iron is catalytically active.

Chapter 3 Catalyst performance

3.1 Introduction

Having modified and impregnated wool fibre, the next phase was to evaluate catalytic activity in a simple system. This was performed in three stages.

Stage 1:	The determination of catalytic activity in a dye system and a phenol system.
Stage 2:	Optimisation of static batch conditions for the oxidation of phenol.
Stage 3:	The determination of catalyst lifetime or longevity.

Stage 1:

Batch-to-batch comparisons of seven wools were carried out by evaluating the catalyst performance towards oxidative decomposition as outlined below:

1. Determination of catalytic activity towards dyes (Acid Blue 45),
2. Determination of catalytic activity towards phenol.

Stage 2:

Optimisation of the static batch conditions for oxidation of phenol. Firstly the amount of hydrogen peroxide was adjusted to allow for complete mineralisation. It was calculated that the concentration of hydrogen peroxide was not sufficient for this to occur. Secondly, the optimum catalyst: phenol ratio was investigated whilst still evaluating homogeneous contribution to catalysis.

Stage 3:

Samples were identified from this static batch study to determine the longevity of the catalyst in a dynamic flow reactor with an aqueous solution of phenol as feed. Other catalysts produced by an improved impregnation technique were included in this studied. The wool catalysts evaluated were as follows:

1. Crossbred wool modified with hydroxylamine and impregnated with Fe (III)
2. DEFRA top wool modified with hydroxylamine and impregnated with Fe (III)
3. Crossbred wool modified with hydroxylamine and impregnated with Fe (III)/Calcium salt
4. Crossbred wool modified with hydroxylamine and impregnated with Fe (III)/lithium salt
5. Dark Grey Herdwick wool modified with hydroxylamine and impregnated with Fe (III)

3.2 Materials and Chemicals

Wool fibre:

Table 3.1 Wool samples investigated including supplier and chemical processing applied.

Wool	Supplier	Chemical Processing at DMU
Mill Scoured Crossbred	Thomas Chadwick & Sons	Modification & Impregnation (Fe^{3+}) Batch 1
	Thomas Chadwick & Sons	Modification & Impregnation (Fe^{3+}) Batch 2
	Thomas Chadwick & Sons	Modification & Impregnation (Fe^{3+}/Ca)
	Thomas Chadwick & Sons	Modification & Impregnation (Fe^{3+}/Li) Batch 1
	Thomas Chadwick & Sons	Modification & Impregnation (Fe^{3+}/Li) Batch 2
Mill Scoured Dark Grey Herdwick	Thomas Chadwick & Sons	Modification & Impregnation (Fe^{3+})
Non Scoured	DEFRA	Scouring, modification & impregnation (Fe^{3+})

Where relevant, samples had been scoured, modified and impregnated using the chemicals and methods outlined in Chapter 2 (Sections 2.3.2, 2.3.3 and 2.3.4)

***Catalysis*:**

Dye Acid Blue 45 (CI 63010) (Aldrich), phenol (Aldrich), hydrogen peroxide, 30% w/v (Aldrich)

***HPLC*:**

C-18 (250 x 4.6mm) column (Hichrom), acetonitrile (HPLC grade, Aldrich), methanol (HPLC grade, Aldrich)

3.3 Methods

3.3.1 Static Batch Evaluation of Catalysis

Many samples as previously described in Chapter 2 were evaluated for catalytic activity in a static batch reactor. Batch-to-batch comparisons of wool samples were carried out to ensure that results were reproducible. Two systems were investigated for both heterogeneous and homogeneous contribution towards catalysis.

1. Determination of catalytic activity towards dyes (Acid Blue 45),
2. Determination of catalytic activity towards phenol.

Determination of heterogeneous activity of the wool catalyst towards Acid Blue 45

The dye, Acid Blue 45 (50ml, 10ppm) was pH adjusted to pH 3 with dilute hydrochloric acid, and 0.5ml of H_2O_2 was added from a stock solution (5000ppm) so that the resultant concentration of H_2O_2 was 50ppm.

Various concentrations of Acid Blue 45 solutions were prepared (1, 2, 5, 7 and 10ppm) for the construction of calibration graph. These samples were then analysed using UV/VIS at λ_{max} = 594nm. This was performed in triplicate.

For the catalysis feed (50ml) was placed in a dreschel bottle and a zero reading taken using UV/VIS at λ_{max} = 594nm. This became the t = 0mins reading. The active wool fibre (0.6g) was added and the vessel stoppered allowing air to flow through (100 $mLmin^{-1}$). Samples were rapidly analysed at five minute intervals for a total of thirty minutes. The apparatus setup is illustrated below in Figure 3.1. Each time a sample was removed for analysis it was then returned to the feed. On completion of the reaction, the wool was removed and rinsed to remove any traces of hydrogen peroxide. Wool samples were subjected to three cycles with no drying cycles between runs. Heterogeneous activity of all samples was determined by measuring the disappearance of dye with time (C_t/C_0). The catalytic activity of all samples was evaluated in duplicate and the results averaged. Control samples (dye solution+H_2O_2+bubbled air, but no wool catalyst) have been evaluated in the same manner.

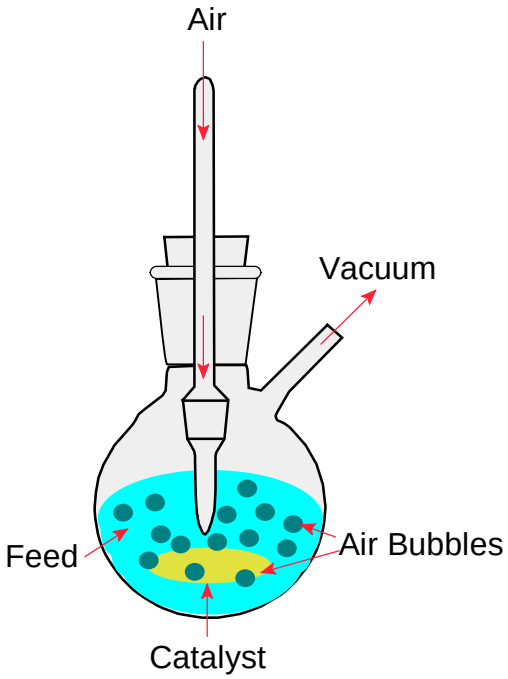


Figure 3.1 Apparatus for catalysis

Phenol decomposition

A solution of phenol (50ml, 24ppm) was pH adjusted to pH 3 with dilute hydrochloric acid. 0.5mL of a stock solution of H_2O_2 (5000ppm) was added to give a resultant H_2O_2 concentration of 50ppm.

Various concentrations of phenol solutions were prepared (5, 10, 15, 20, 25 and 30ppm) and analysed by HPLC for the calibration graph. A standard C-18 (250 x 4.6mm) packed column was used as the stationary phase. The mobile phase was a mixture of water (40% v/v) and methanol (60% v/v) at a flow rate of 1 ml/min. The column elute was passed through a UV detector set at 254nm. Sample volumes of 20µl were injected onto the column. Samples were analysed in triplicate.

For the catalysis feed (50ml) was placed in a dreschel bottle and a zero reading taken for analysis, this became the t = 0mins reading. The active wool fibre (0.6g) was added and the vessel stoppered allowing air to flow through. Samples were collected at ten minute intervals for a total of sixty minutes. The apparatus was identical to that described in Figure 3.1. Once complete, the wool was removed and rinsed to remove any traces of hydrogen peroxide.

Each sample collected was analysed by HPLC, using the same column as for calibration. The mobile phase was a mixture of water (40% v/v) and methanol (60% v/v) at a flow rate of 1 ml/min. UV detection and volume of sample injection were as for calibration above, allowing for phenol disappearance to be determined (C_t/C_0). A control (phenol solution + H_2O_2 + bubbled air, but no wool catalyst), has been used to evaluate the hydrogen peroxide contribution to catalysis using the same setup. Wool samples with no Fe (III) impregnation have been evaluated in the same manner.

Test for homogeneous catalysis

On completion of a catalysis cycle, the treated feed (dye or phenol solution) was kept and the wool removed. Untreated feed prepared as previously described was then added to the treated feed. A sample was taken for analysis using UV/VIS at λ_{max} = 594nm (for the dye) or HPLC technique (for phenol) in order to determine the resultant

concentration of the dye or phenol in the feed. This became the t = 0 mins reading for the homogeneous test. The vessel was then stoppered to allow air flow as before. Samples were analysed at regular intervals, and again each time a sample had been analysed it was returned to the feed giving the concentration at that time for the dye or phenol. Wool catalyst samples were subjected to homogeneous testing over three cycles. The homogeneous activity (C_t/C_0) of all samples was evaluated multiple times and the results averaged.

Catalytic activity after dye sorption on wool

This study was performed under static conditions on two samples, hydroxylamine and 50:50 mixture modified and Fe (III) impregnated wools. Concentrated dye solution (25ml, 1g/l) and distilled water (25ml) containing the wool sample (0.3g) adjusted to pH 3 were each degassed with nitrogen (4 hours) to displace dissolved oxygen from the solutions. The degassed dye solution was then added to the flask containing the wool sample in degassed water and left under a nitrogen environment (for a further 4 hours). After sorption was complete, the fibre was thoroughly washed with water and dried at room temperature. Once dry, each sample was evaluated for heterogeneous and homogeneous catalysis towards dye in the same way as previously.

3.3.2 Catalyst Longevity

The aim of this study was to determine the longevity of the catalyst in a dynamic flow reactor with an aqueous solution of phenol as feed. Samples of wool catalyst that were evaluated were as follows:

1. Crossbred wool modified with hydroxylamine and impregnated with Fe (III)
2. DEFRA wool modified with hydroxylamine and impregnated with Fe (III)
3. Crossbred wool modified with hydroxylamine and impregnated with Fe (III)/calcium salt
4. Crossbred wool modified with hydroxylamine and impregnated with Fe (III)/lithium salt

5. Dark Grey Herdwick wool modified with hydroxylamine and impregnated with Fe (III)

In static batch experiments poor heterogeneous catalyst activity was achieved with high levels of homogeneous contribution to catalysis by Dark Grey Herdwick samples. As this was the cheapest wool investigated it was hoped that the homogeneous levels may decrease over a prolonged period of catalysis and it was also hoped that the heterogeneous contribution to catalysis may improve. To evaluate this, a dynamic study would be required.

Analysing the homogeneous contribution to catalysis is not possible in the conventional manner when using a dynamic setup. Samples can however be extracted at regular intervals and analysed using AAS for iron in solution. Any iron detected in solution would result in a level of homogeneous catalysis.

In previous static studies 24ppm solutions of phenol (50ml) were decomposed within 60 minutes. The amount of wool catalyst used in static studies was ~0.6g of wool catalyst. For the dynamic studies it was desirable to reduce the retention time within the reactor to 30 minutes to prevent the length of each study extending into days. This was made possible by setting the reactor volume to 60ml ensuring that at a flow of 2 ml min^{-1} the feed would be in contact with the catalyst for 30 minutes. The amount of wool catalyst used in the dynamic studies was calculated using the following steps:

- Static studies – Volume was 50ml, wool catalyst amount was 0.6 g and reaction length 60 minutes.
- Using the above parameters, the reaction time can be reduced to 30 minutes by increasing the wool catalyst amount to 1.2g (double).
- Dynamic studies – Increasing the volume to be 60ml, then the amount of wool catalyst becomes

$$\frac{60}{50} \times 1.2g = 1.44g$$

- This amount was increased to ~2.0g to further ensure that the retention time 30 minutes enabled complete decomposition of phenol.

Dynamic catalysis evaluation

Wool catalyst samples (2g) were placed in the reactor with bubbled air (45 ml min^{-1}) measured and controlled by a flow meter. A continuous flow of phenol solution (24ppm) containing hydrogen peroxide (50ppm) was pumped through the reactor at a flow of 2 ml min^{-1}. Samples were taken from the reactor outlet at regular time intervals and analysed for phenol by HPLC using the conditions outlined. The sample times were 5, 15, 30, 90, 120, 150, 180, 210, 240, 300 minutes and then every 60 minutes until deactivation occurred. Multiple samples from the same production batch were evaluated where deemed necessary. Iron leaching into solution was investigated throughout catalysis by measurement with AAS.

Iron determinations were carried out for wool samples prior to catalysis and after deactivation using AAS.

3.3.3 Optimisation of parameters of catalysis

There were two objectives to this work. The first was to adjust the amount of hydrogen peroxide to allow for complete mineralisation. In previous experiments it was calculated that the concentration of hydrogen peroxide was not sufficient for this to occur. Calculations were performed to identify the required amount and are shown below.

Hydrogen Peroxide Calculation:

$$C_6H_6O + 7O_2 \rightarrow 6CO_2 + 3H_2O$$

$$14H_2O_2 \rightarrow 14H_2O + 7O_2$$

The equation demonstrates that 14 moles of H_2O_2 (14 x 34 mg/l = 476 mg/l) would be required to mineralise 1 mole of phenol (94 mg/l). In our experiments we have used 24ppm phenol; therefore the required amount of hydrogen peroxide was as follows,

$$\frac{476}{94} \times 24 = 121.5 mg/l$$

For all future catalysis experiments involving phenol a minimum of 121.5 mg/l of H_2O_2 was applied. This assumes that every $OH^{\cdot}$ is used to mineralise the phenol. In practice this will not be so, as the extremely reactive radical will react with H_2O_2, Fe^{3+}.

The second objective was to investigate the optimum catalyst: phenol ratio. This was performed by static evaluation of catalytic activity with differing amounts of wool catalyst. Homogeneous contribution to catalysis was also determined at appropriate stages of the study.

Catalytic Evaluation:
Various concentrations of phenol solutions were prepared (5, 10, 15, 20, 25 and 30ppm) and analysed by HPLC for the calibration graph. The HPLC conditions were as previously described in section 3.3.1.

For catalytic activity the amount of wool catalyst used was varied (0.2-1.2g). The experimental procedure was the same as that outlined previously. Samples were extracted every 10 minutes and analysed by HPLC (λ_{max}=254nm) until phenol was no longer detected.

3.4 Results and Discussion

3.4.1 Static batch evaluation of catalysis

Evaluation of catalytic activity towards dye

All wool samples used for the evaluation of the decolourisation of Acid Blue 45 were obtained from the DEFRA top wool having undergone laboratory non-ionic scouring, modification at pH9.5 and impregnation. The results obtained for the catalytic decomposition of Acid Blue 45 are given in Table 3.2 followed by catalysis results after a preliminary dye sorption study data presented in Table 3.3. All wools modified and impregnated with hydroxylamine or a 50:50 mixture (hydroxylamine and hydrazine) were subjected to the sorption study.

Table 3.2 Acid blue 45 decomposition data using DEFRA wool samples over three cycles to determine the heterogeneous and homogeneous activity

Sample	Decomposition of Acid Blue 45 (%)					
	1st Cycle		2nd Cycle		3rd Cycle	
	Het.	Hom.	Het.	Hom.	Het.	Hom.
Scoured (non-modified) + Fe^{3+}	86	72	53	22	2	0
Hydrazine Modified + Fe^{3+}	100	75	100	82	100	71
Hydroxylamine Modified + Fe^{3+}	85	20	81	15	95	20
50:50 Modified + Fe^{3+}	100	34	100	37	100	39
Blank (No wool catalyst present)	1	-	-	-	-	-
No air (wool catalyst present)	53	-	-	-	-	-

[Acid Blue 45] = 10ppm, 50ml, [H_2O_2] = 50ppm, 0.6g wool catalyst, 30 minutes

Table 3.3 Acid Blue 45 decomposition after preliminary dye sorption step for DEFRA wools modified with hydroxylamine and a 50:50 mixture

Sample	Decomposition of Acid Blue 45 (%)					
	1st Cycle		2nd Cycle		3rd Cycle	
	Het.	Hom.	Het.	Hom.	Het.	Hom.
Hydroxylamine Modified + Fe^{3+}	19	2	29	1	29	3
50:50 Modified + Fe^{3+}	0	0	53	0	57	0

[Acid Blue 45] = 10ppm, 50ml, [H_2O_2] = 50ppm, 0.6g wool catalyst, 30 minutes

Both heterogeneous and homogeneous catalysis appear to be present in all wool samples, regardless of the type of chemical modification or whether modification was used. It was observed that sorption took place during catalysis, as the wool became blue in colour and remained blue after washing. The unmodified wool impregnated with Fe (III) leaches Fe (III) into solution so that most of the catalysis occurs in the homogeneous phase which is identified from the homogeneous results given in Table 3.2. As there is no catalyst present during the cycle for homogeneous evaluation the source of iron can only be that which has leached into solution from the previous heterogeneous cycle. Catalysis stops after the second cycle as the wool no longer contains Fe (III) to initiate catalysis. It was very difficult to determine how much of the dye reduction was as a result of catalysis, hence the need for sorption testing (Table 3.3) which is discussed later.

The modified wools perform better with 81-100% decolourisation of the dye in 30 minutes over the three cycles tested. However, the wool sample modified with hydrazine shows considerable homogeneous activity arising from continuous but sustained leaching of the Fe (III) off the wool.

The hydroxylamine modification gives the least homogeneous activity which is sustained at 20% decolourisation over the three cycles. Although not all dye was decolourised in 30 minutes. 100% decolourisation could be achieved over a longer period of time.

It was found that following sorption of dye (from an excess concentrated solution of the dye) the hydroxylamine modified Fe (III) impregnated wool behaved poorly as a catalyst whilst exhibiting little homogeneous activity considering the low level of heterogeneous contribution to catalysis (Table 3.3). The 50:50 modified wool showed an increase from 0% dye decolourisation on the 1st cycle to 53-57% decolourisation on the 2nd and 3rd cycle. It can be seen that there was no homogeneous activity (Fe (III) leaching) from the 50:50 hydroxylamine / hydrazine modified Fe (III) impregnated wool. Thus after sorption of dye, neither the hydroxylamine or 50:50 mixture hydroxylamine / hydrazine modified wool catalysts performed well.

It was thought that a dye system may not be best for evaluating the catalytic activity of Fe (III) impregnated and modified wool. Many dye-systems are used industrially for the dyeing of wool fibre. Acid Blue 45 belongs to the anthraquinone group of dyes used in the dyeing of wool and protein fibres in acid solutions. Such dyes usually have a good light and wet fastness (CEGARRA et al., 1999). Wet fastness relates to the how strongly the dye is held on the wool, i.e. the ability for the dye to remain permanent and not run or fade. A more straightforward evaluation of catalytic activity could be determined with the use of an alternate system, for example, phenol, where sorption to the wool will be weaker as there are fewer functional groups and the molecule is not charged, unlike Acid Blue 45. It is for this reason that the substrate was changed to phenol in this preliminary evaluation of catalytic activity by a range of modified wool fibres.

Evaluation of catalytic activity towards a phenol system

The samples investigated are given in Table 3.4. Two modifications, that is, the 50:50 hydrazine/hydroxylamine and hydroxylamine modified wools (both modified at pH = 7) were the subject of this evaluation.

Table 3.4 Wool catalysts evaluated for phenol decomposition

Sample No.	Wool Type	Processing
1	Woolmark (Industrially Processed)	Laboratory Scoured, 50:50 Modified & Fe (III) Impregnated
2	Woolmark (Industrially Processed)	Laboratory Scoured, Hydroxylamine Modified & Fe (III) Impregnated
3	Woolmark (Industrially Processed)	Laboratory Scoured & Fe (III) Impregnated
4	Woolmark (Industrially Processed)	Non-Scoured & Fe (III) Impregnated
5	DEFRA	Laboratory Scoured, 50:50 Modified & Fe (III) Impregnated
6	DEFRA	Laboratory Scoured, Hydroxylamine Modified & Fe (III) Impregnated
7	DEFRA	Laboratory Scoured & Fe (III) Impregnated
8	DEFRA	Non-Scoured & Fe (III) Impregnated
9	Dark Grey Herdwick	Mill Scoured 50:50 Modified & Fe (III) Impregnated
10	Dark Grey Herdwick	Mill Scoured Hydroxylamine Modified & Fe (III) Impregnated
11	Dark Grey Herdwick	Mill Scoured & Fe (III) Impregnated
12	Dark Grey Herdwick	Non-Scoured & Fe (III) Impregnated
13	Dark Grey Herdwick	Laboratory Scoured 50:50 Modified & Fe (III) Impregnated
14	Dark Grey Herdwick	Laboratory Scoured Hydroxylamine Modified & Fe (III) Impregnated
15	Dark Grey Herdwick	Laboratory Scoured & Fe (III) Impregnated
16	Swaledale	Mill Scoured 50:50 Modified & Fe (III) Impregnated
17	Swaledale	Mill Scoured Hydroxylamine Modified & Fe (III) Impregnated
18	Swaledale	Mill Scoured & Fe (III) Impregnated
19	Swaledale	Non-Scoured & Fe (III) Impregnated
20	Swaledale	Laboratory Scoured 50:50 Modified & Fe (III) Impregnated
21	Swaledale	Laboratory Scoured Hydroxylamine Modified & Fe (III) Impregnated
22	Swaledale	Laboratory Scoured & Fe (III) Impregnated
23	Crosses	Laboratory Scoured Hydroxylamine Modified & Fe (III) Impregnated
24	Crosses	Industrially Scoured Hydroxylamine Modified & Fe (III) Impregnated
25	Halfbreds	Laboratory Scoured Hydroxylamine Modified & Fe (III) Impregnated
26	Blackface	Laboratory Scoured Hydroxylamine Modified & Fe (III) Impregnated

[Phenol] = 24ppm, [H_2O_2] = 50ppm, Wool = 0.6g, [Fe] = Variable

Samples were scoured, modified (where relevant), and impregnated using the methods outlined in Section 2.1.2. Additionally, batch-to-batch repeats were performed to evaluate the wool

catalysts performance over three cycles. Results for control samples are given in Table 3.5.

Table 3.5 Phenol decomposition achieved using control samples (no impregnation)

Wool Type	Processing	% Phenol Decomposition
Woolmark [a]	50:50 Modified & No Fe (III) Impregnation	20.5 – 21.5%
Woolmark [a]	Hydroxylamine Modified & No Fe (III) Impregnation	21.0 – 22.5%
Woolmark [a]	Laboratory Scoured & No Fe (III) Impregnation	22.5 – 23.0%
DEFRA [a]	50:50 Modified & No Fe (III) Impregnation	21.0 – 22.0%
DEFRA [a]	Hydroxylamine Modified & No Fe (III) Impregnation	22.5 – 23.5%
DEFRA [a]	Laboratory Scoured & No Fe (III) Impregnation	22.0 – 23.0%
Dark Grey Herdwick [a]	Mill Scoured & No Fe (III) Impregnation	23.0 – 24.0%
Dark Grey Herdwick [a]	Mill Scoured 50:50 Modified & No Fe (III) Impregnation	24.0 – 25.0%
Dark Grey Herdwick [a]	Mill Scoured Hydroxylamine Modified & No Fe (III) Impregnation	22.0 – 23.5%
Swaledale [b]	Laboratory Scoured Hydroxylamine Modified No Fe (III) Impregnation	5.5 – 6.5%
Swaledale [b]	Laboratory Scoured 50:50 Modified No Fe (III) Impregnation	30.5 – 32.0%
Swaledale [b]	Industrially Scoured Hydroxylamine Modified No Fe (III) Impregnation	10.0 – 11.0%
Swaledale [b]	Industrially Scoured 50:50 Modified No Fe (III) Impregnation	7.5 – 8.5%
No Wool Catalyst [a]	Phenol, Hydrogen Peroxide (50ppm) and bubbled Air	25.5 – 26.5%

(a) Calibration equation used for phenol determination was: $y = 34772x$
(b) Calibration equation used for phenol determination was: $y = 0.3464x$
[Phenol] = 24ppm, Wool = 0.6g, [Fe] = Variable

As can be seen in Table 3.5, the extent of phenol decomposition by all the control wool samples (no Fe (III) impregnation) was similar, generally between 6-32% decomposition. It can also be seen that the blank cycle (phenol + hydrogen peroxide + bubbled air) gives a phenol decomposition of 26%. Therefore, it can be concluded that

all wools prior to impregnation have no influence on catalysis, thus reduction in phenol is as a result of catalysis. The catalytic activity results from the batch-to-batch studies are displayed for all wools in Table 3.6.

Table 3.6 Percentage (%) phenol decomposition using Woolmark and DEFRA catalyst samples

Sample	1st Cycle Het.			1st Cycle Hom.	2nd Cycle Het.			2nd Cycle Hom.	3rd Cycle Het.			3rd Cycle Hom.
Repeat Batch Number	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**
WOOLMARK [a]												
Lab. Scoured 50:50 Modified & Fe (III) Impregnated	99	99	99	7	98	98	81	4	98	98	98	7
Lab. Scoured Hydroxylamine Modified & Fe (III) Impregnated	99	100	99	11	100	100	100	10	100	100	100	10
Laboratory Scoured & Fe (III) Impregnated	99	56	-	11	100	52	-	10	100	60	-	10
Non-Scoured & Fe (III) Impregnated	36	31	-	37	49	49	-	47	48	49	-	51
DEFRA [b]												
Lab. Scoured 50:50 Modified & Fe (III) Impregnated	93	93	93	22	93	93	93	21	93	94	94	37
Lab. Scoured Hydroxylamine Modified & Fe (III) Impregnated	99	99	99	10	99	99	99	17	99	99	99	20
Laboratory Scoured & Fe (III) Impregnated	54	53	-	41	47	56	-	39	50	51	-	39
Non-Scoured & Fe (III) Impregnated	48	50	-	36	47	50	-	37	45	45	-	40

(a) WOOLMARK – Calibration equation used for phenol determination was: y = 34762x
(b) DEFRA – Calibration equation used for phenol determination was y = 35138x
[Phenol] = 24ppm, [H_2O_2] = 50ppm, Wool = 0.6g, [Fe] = Variable, time = 60 minutes

Both the Woolmark and DEFRA wools modified with hydroxylamine or 50:50 mixture of hydroxylamine: hydrazine resulted in good catalysts able to decompose ~100% phenol in 60 minutes, with excellent batch reproducibility demonstrated for each repeat over the three cycles (Table 3.6). The contribution from homogeneous catalysis (i.e. Fe(III) leaching off the wool) was low from 4-37%. The unmodified Woolmark and DEFRA wools behaved poorly with a large contribution from homogeneous catalysis. From Table 3.7 and Table 3.8 it can be seen that both the Swaledale and Dark Grey Herdwick wool behaved similarly.

The hydroxylamine modified Herdwick sample gave an unexpectedly poor result with phenol decomposition (see Table 3.7) arising mostly from homogeneous catalysis. The 50:50 hydroxylamine : hydrazine modified sample performed better with 100% phenol decomposition reproducible over three cycles and three batches, but the homogeneous contribution was somewhat higher than the corresponding Woolmark and DEFRA samples at between 26-39% for the mill scoured samples but between 54-100% for the laboratory scoured samples. This difference between the mill and laboratory scoured samples was due to the difficulty in obtaining a uniformly representative sample of this wool for batch testing as it comprised of a mixture of coloured and non-coloured fibres intimately interwoven which were not evenly distributed within the samples. It contains a very high proportion of grease on its outer surface before scouring, high percentage of melanin in the fibres; it is coarser and breaks on handling to a greater extent than the other wools. A larger number of samples would help eliminate this problem.

Table 3.7 Percentage (%) phenol decomposition using Dark Grey Herdwick wool catalyst samples

Sample	1st Cycle Het.			1st Cycle Hom.	2nd Cycle Het.			2nd Cycle Hom.	3rd Cycle Het.			3rd Cycle Hom.
Batch Number	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**
Dark Grey Herdwick [c]												
Mill Scoured 50:50 Modified & Fe (III) Impregnated	100	100	100	26	100	100	100	39	100	100	100	37
Mill Scoured Hydroxylamine Modified & Fe (III) Impregnated	26	31	26	48	23	33	31	41	24	28	23	32
Mill Scoured & Fe (III) Impregnated	34	30	-	49	-	-	-	-	-	-	-	-
Non-Scoured & Fe (III) Impregnated	33	38	-	56	-	-	-	-	-	-	-	-
Lab. Scoured 50:50 Modified & Fe (III) Impregnated	26	100	-	54	29	100	-	75	85	100	-	100
Laboratory Scoured Hydroxylamine Modified & Fe (III) Impregnated	100	100	-	100	100	100	-	100	85	100	-	100
Lab. Scoured & Fe (III) Impregnated	69	100	-	100	-	-	-	-	-	-	-	-

(c) Dark Grey Herdwick – Calibration equation used for phenol determination was: y = 0.9933x
[Phenol] = 24ppm, [H_2O_2] = 50ppm, Wool = 0.6g, [Fe] = Variable, time = 60 minutes

Table 3.8 showed that in general the Swaledale wool samples had high levels of homogeneous activity. The results given in Table 3.8 indicated that in most cases, any phenol decomposition was solely due to homogeneous catalysis. This was not the case for non-scoured and Fe(III) impregnated wool, as the catalytic activity was poor with a maximum phenol decomposition of 45% being achieved. It was noticed that when the Swaledale samples had been chemically modified, the batch-to-batch reproducibility was good. This was also noticed in the other wool samples (e.g. DEFRA), emphasising

the necessity for chemical modification. It is thought that the poor performance of this wool was due to the presence of the pigmented fibres, thus a higher melanin content.

Table 3.8 Percentage (%) Phenol Decomposition using Swaledale Wool Catalyst Samples

Sample	1st Cycle Het.			1st Cycle Hom.	2nd Cycle Het.			2nd Cycle Hom.	3rd Cycle Het.			3rd Cycle Hom.
Batch Number	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**
Swaledale [d]												
Mill Scoured 50:50 Modified & Fe (III) Impregnated	40	45	-	35	76	73	-	18	90	85	-	62
Mill Scoured Hydroxylamine Modified & Fe (III) Impregnated	21	29	-	100	96	89	-	100	100	100	-	100
Mill Scoured & Fe (III) Impregnated	63	45	-	62	-	-	-	-	-	-	-	-
Non-Scoured & Fe (III) Impregnated	24	46	-	5	-	-	-	-	-	-	-	-
Lab. Scoured 50:50 Modified & Fe (III) Impregnated	27	29	-	13	53	53	-	3	34	36	-	6
Lab. Scoured Hydroxylamine Modified & Fe (III) Impregnated	30	46	-	13	40	43	-	22	37	39	-	5
Lab. Scoured & Fe (III) Impregnated	31	25	-	20	-	-	-	-	-	-	-	-

(d) Swaledale – Calibration equation used for phenol determination was: y = 0.1076x
[Phenol] = 24ppm, [H_2O_2] = 50ppm, Wool = 0.6g, [Fe] = Variable, time = 60 minutes

Experiments using hydroxylamine modified and Fe (III) impregnated Crossbred wool (Table 3.9) indicated that between 98% and 100% phenol decomposition could be achieved by the third cycle using either laboratory or industrially scoured samples. The homogeneous contribution was found to be less than 6% and at best only 1% by the third cycle. It was also observed that the wool acted poorly as a catalyst for the first two cycles, particularly the first cycle, indicating conditioning of the catalyst during the first two hours. This was also seen for the Halfbreds and Blackface catalyst samples which

were treated and evaluated in the same way. The maximum phenol decompositions achieved using these samples were 83% and 82%, respectively. Homogeneous contribution over the three cycles was less than 22% for the Halfbreds and 32% for the Blackface, improving on the third cycle to 16% and 5% respectively. Excellent batch-to-batch reproducibility was found in all three wools.

Table 3.9 Percentage (%) Phenol Decomposition using Thomas Chadwick Wool Catalyst Samples

Sample	1st Cycle Het.			1st Cycle Hom.	2nd Cycle Het.			2nd Cycle Hom.	3rd Cycle Het.			3rd Cycle Hom.
Batch Number	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**	**1**	**2**	**3**	**Avg.**
Crossbred [e]												
Lab. Scoured Hydroxylamine Modified & Fe (III) Impregnated	65	62	-	18	83	87	-	11	98	100	-	6
Mill Scoured Hydroxylamine Modified & Fe (III) Impregnated	28	25	-	2	89	89	-	2	98	98	-	1
Halfbreds [f]												
Lab. Scoured Hydroxylamine Modified & Fe (III) Impregnated	11	14	-	4	16	11	-	22	82	84	-	16
Blackface [g]												
Lab. Scoured Hydroxylamine Modified & Fe (III) Impregnated	43	42	-	12	53	49	-	32	83	82	-	5

(e) Crossbred – Calibration equation used for phenol determination was: y = 0.445x
(f) Halfbreds – Calibration equation used for phenol determination was: y = 0.2771x
(g) Blackface – Calibration equation used for phenol determination was: y = 0.2771x

The heterogeneous catalysis results for Crossbred mill scoured, modified with hydroxylamine and Fe (III) impregntated (batch 1) are presented graphically in Figure 3.2. It was observed that the sample was initially very slow during catalysis. This was attributed to the wettability of wool and it was suspected that the initial catalysis performance could be improved with pre-wetting of the samples.

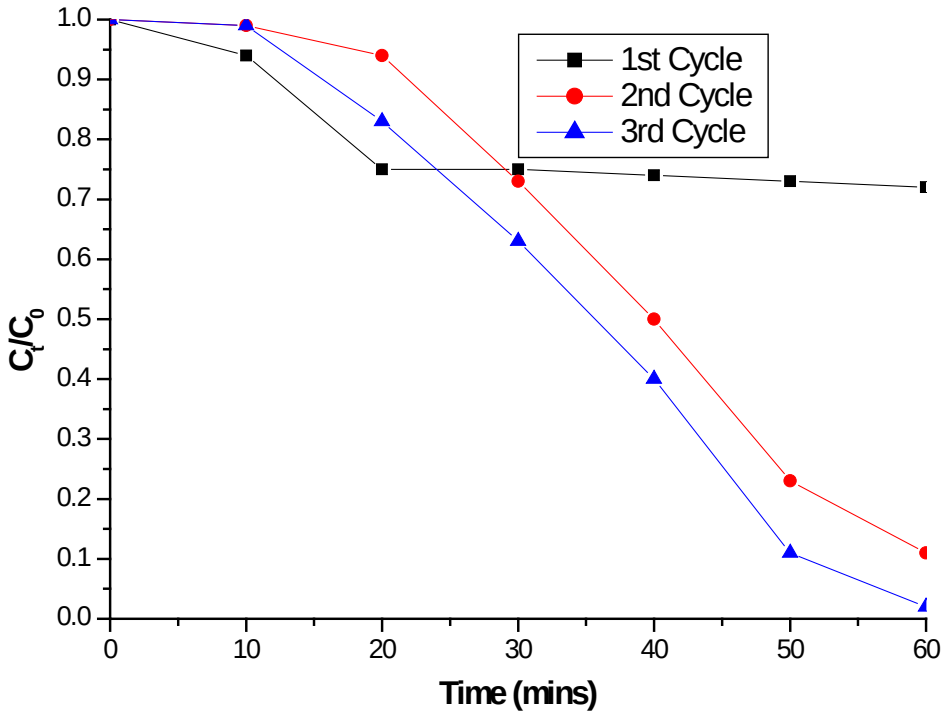


Figure 3.2 Heterogeneous catalysis for the decomposition of phenol over three cycles by Crossbred mill scoured, hydroxylamine modified and Fe (III) impregnated wool, [Phenol] = 24ppm, vol = 50mL, [Fe content] = 0.074mmol/g wool, pH = 3, [H_2O_2] = 50ppm and wool = 0.6g

3.4.2 Catalyst longevity

Two batches of Crossbred modified and Fe (III) impregnated were investigated, whereas only one DEFRA batch was evaluated as it gave similar results to the equivalent Crossbred sample. Catalyst lifetimes were improved by using the impregnation solutions containing Fe (III)/calcium and Fe (III)/lithium salts, with the latter being investigated further for reproducibility. Only one batch of the Dark Grey Herdwick (DGH) catalyst was evaluated as it did not perform well with iron leaching into solution. The data for all studies can be found in Appendix 3 - Dynamic Studies Data for Crossbred, DEFRA and Dark Grey Herdwick Wool Catalysts and is represented graphically in Figure 3.3 and Figure 3.4.

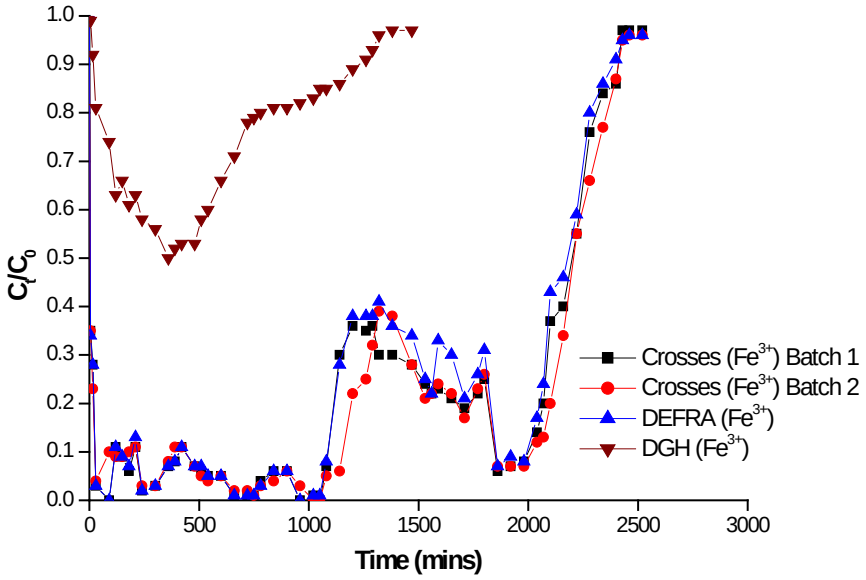


Figure 3.3 Phenol Decomposition during the Dynamic Studies for Crossbred, DEFRA and Dark Grey Herdwick wools hydroxylamine modified and Fe (III) impregnated, [Phenol] = 24ppm, Flow = 2 ml/min, [Fe content] = Variable, pH = 3, [H_2O_2] = 50ppm and wool = 2g

It can be identified from Figure 3.3 that longevity does not appear to be affected by wool type. Both the hydroxylamine modified and impregnated Crossbred and DEFRA catalysts follow the same pattern. Batch reproducibility was also good. Catalyst lifetime was found to be around 42 hours. However, lifetime for the Dark Grey Herdwick wool catalyst was short (24.5 hours) and on further analysis it was found that iron could be detected in solution throughout the catalysis process.

When using the improved impregnation technique (Fe^{3+}/Li^{+} or Fe^{3+}/Ca^{2+}) it can be observed that the catalyst lifetime was increased from 42 hours to 49 hours (Ca^{2+}) and 60 hours (Li^{+}) (see Figure 3.4). Impregnation with co-salts improves the catalyst. This is related to the anion helping reduce the positive charge of the complex.

$$[Fe(H_2O)_6]^{3+} + Cl^{-} \rightleftharpoons [Fe(H_2O)_5Cl]^{2+} + H_2O$$

The NH_2 groups become protonated repelling the positively charged complex, therefore increasing anion concentration and reducing complex charge helps the complex.

Following impregnation with co-salts, the catalytically active iron can be influenced by salt effect or 'kinetic salt effects'.

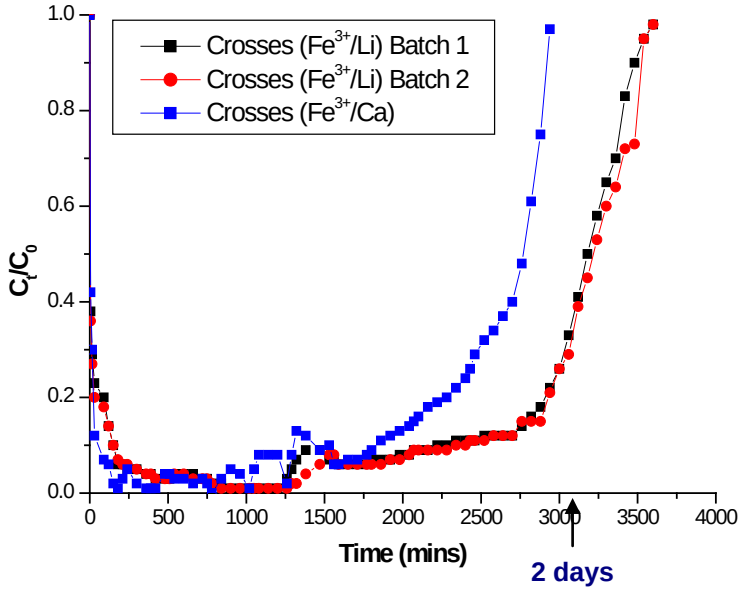


Figure 3.4 Phenol Decomposition during the Dynamic studies for hydroxylamine modified Crossbred wool samples impregnated with Fe (III)/calcium salt or Fe (III)/lithium salt, [Phenol] = 24ppm, Flow = 2 ml/min, [Fe content] = Variable, pH = 3, [H_2O_2] = 50ppm and wool = 2g

The iron content was determined for each sample before catalysis and after deactivation. Samples of the solution post catalysis were also evaluated for iron to determine if iron was leaching, thus contributing to homogeneous activity. Table 3.10 displays all iron content results for each wool study. After deactivation the iron content of the catalyst was reduced by approximately 50% compared with less than 5% for all other catalysts (Table 3.10).

Table 3.10 Iron content data determined by AAS for each dynamic study

Sample	Fe Content (mmol / g wool)		Difference in Fe Content (%)	Max. Fe content in solution during catalysis (ppm)
	Before catalysis	Post catalysis		
Crossbred (Fe^{3+}) (1)	0.0738	0.0757	+2.6	N.D
Crossbred (Fe^{3+}) (2)	0.0811	0.0795	-2.0	N.D
Crossbred (Fe^{3+}/Ca^{2+})	0.0804	0.0780	-3.0	N.D
Crossbred (Fe^{3+}/Li^{+}) (1)	0.0791	0.0816	+3.2	N.D
Crossbred (Fe^{3+}/Li) (2)	0.0791	0.0807	+2.0	N.D
DEFRA (Fe^{3+})	0.0877	0.0869	-0.9	N.D
DGH (Fe^{3+})	0.0543	0.0263	-51.57	9.09

N.D = No iron detected within the limits of the AAS used

The positive gain in iron after catalysis indicates that the iron distribution is within this range.

3.4.3 Optimisation of catalysis

A control sample was evaluated to investigate the decomposition of phenol by hydrogen peroxide alone (Table 3.11). 34% of phenol reduction was attributed to oxidation with H_2O_2 (no catalyst present). This factor was taken into account when analysing the phenol reduction obtained when using the wool catalyst. The results obtained from the first cycle of catalysis are given in Table 3.12 to Table 3.15.

Table 3.11 Control sample (phenol and hydrogen peroxide only – no catalyst)

Time (mins)	Phenol C_t/C_0
0	1.00
10	0.87
20	0.74
30	0.72
40	0.70
50	0.69
60	0.68
70	0.66

[Phenol] = 24ppm, [H_2O_2] = 122ppm, time = variable

Table 3.12 Phenol decomposition during first cycle heterogeneous catalysis (run 1)

Time	C_t/C_0 using wool catalyst (g)				
(mins)	**0.2**	**0.4**	**0.8**	**1.0**	**1.2**
0	1.00	1.00	1.00	1.00	1.00
10	0.68	0.62	0.71	0.57	0.61
20	0.50	0.43	0.59	0.15	0.54
30	0.34	0.23	0.52	0.04	0.12
40	0.18	0.13	0.07	0.04	0.05
50	0.15	0.09	0.05	0.00	0.03
60	0.10	0.06	0.00	0.00	0.00
70	0.06	0.00	-	-	-
80	0.00	-	-	-	-

[Phenol] = 24ppm, [H_2O_2] = 122ppm, Wool = variable, [Fe] = Variable, time = variable

Initially single cycle static batch comparisons were made to identify the optimum amount of wool catalyst to be used for phenol decomposition. The results obtained are given in Table 3.12 and Table 3.13. Table 3.12 clearly demonstrates that when using 1.0g of wool catalyst complete disappearance of phenol was achieved after 50 minutes compared with over 60 minutes when using 0.6g wool catalyst (see section 3.4.1, Table 3.7). This was the optimum time repeatedly obtained during this study. When using 1.2g of wool catalyst it can be observed that there is a reduction in catalyst performance. This can be attributed to scavenging of the hydroxyl radical by the iron.

Table 3.13 Phenol decomposition during first cycle heterogeneous catalysis (run 2)

Time (mins)	C_t/C_0 using wool catalyst (g)				
	0.2	**0.4**	**0.8**	**1.0**	**1.2**
0	1.00	1.00	1.00	1.00	1.00
10	0.69	0.62	0.71	0.58	0.60
20	0.50	0.42	0.59	0.15	0.54
30	0.34	0.23	0.52	0.04	0.12
40	0.18	0.13	0.07	0.04	0.05
50	0.16	0.09	0.05	0.00	0.03
60	0.10	0.08	0.00	0.00	0.00
70	0.06	0.00	-	-	-
80	0.00	-	-	-	-

[Phenol] = 24ppm, [H_2O_2] = 122ppm, Wool = variable, [Fe] = Variable, time = variable

Table 3.14 and Table 3.15, show the results of homogeneous contribution to catalysis during the first cycle. When using 0.4g wool catalyst this afforded to 12% phenol reduction after 70 minutes, whereas, 1.0g wool catalyst reduced phenol by 6% after 60 minutes (see section 3.4.1, Table 3.7). This is a very positive result indicating that no or very little iron is leaching into solution. In addition these results are reproducible.

Table 3.14 Phenol decomposition during first cycle homogeneous catalysis (run 1)

Time (mins)	C_t/C_0 using wool catalyst (g)	
	0.4	**1.0**
0	1.00	1.00
10	1.00	0.99
20	1.00	0.98
30	0.98	0.97
40	0.95	0.96
50	0.95	0.95
60	0.94	0.94
70	0.88	-

[Phenol] = 24ppm, [H_2O_2] = 122ppm, Wool = variable, [Fe] = Variable, time = variable

Table 3.15 Phenol decomposition during first cycle homogeneous catalysis (run 2)

Time (mins)	C_t/C_0 using wool catalyst (g)	
	0.4	1.0
0	1.00	1.00
10	0.99	0.99
20	0.98	0.99
30	0.97	0.96
40	0.96	0.95
50	0.96	0.94
60	0.96	0.94
70	0.91	-

[Phenol] = 24ppm, [H_2O_2] = 122ppm, Wool = variable, [Fe] = Variable, time = variable

It was found that the most efficient removal of phenol was achieved using 1.0g wool catalyst with complete disappearance of phenol after 50 minutes. The homogeneous contribution to catalysis was also low at a maximum of 6% over the first cycle. The first cycle results are summarised graphically in Figure 3.5.

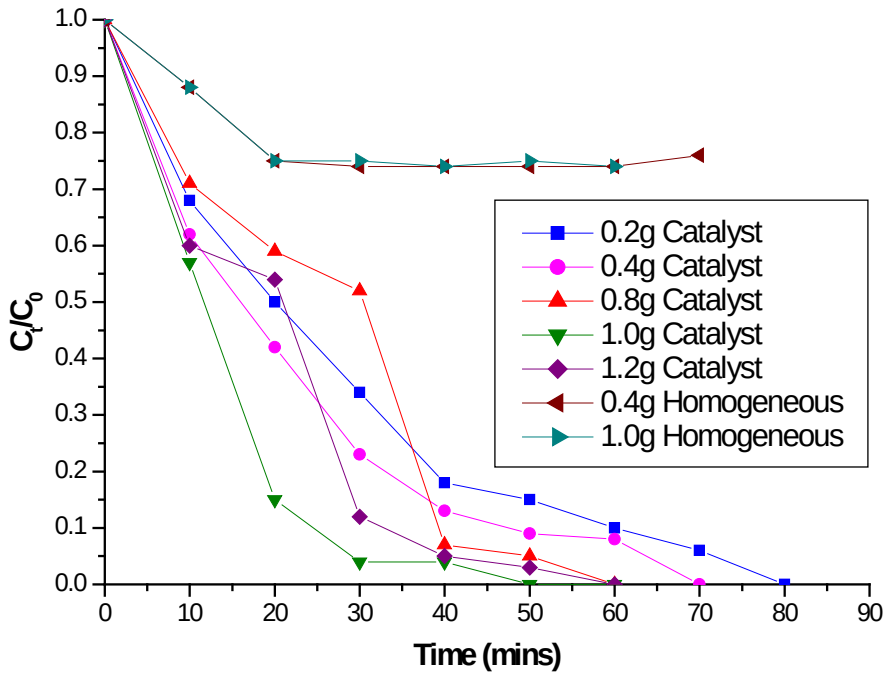


Figure 3.5 Phenol decomposition (C_t/C_0) after the first cycle of catalysis with phenol

A further two cycles of catalysis was performed with 1.0g of wool catalyst. The results obtained are given in Table 3.16 and illustrated graphically in Figure 3.6.

Table 3.16 Phenol decomposition (C_t/C_0) obtained for the 2nd and 3rd cycles of catalysis with 1.0g of wool catalyst

Time (mins)	2nd Cycle		3rd Cycle	
	Het	Hom	Het	Hom
0	1.00	1.00	1.00	1.00
10	0.77	0.99	0.82	0.99
20	0.35	0.99	0.31	0.97
30	0.17	0.98	0.19	0.96
40	0.05	0.98	0.06	0.96
50	0.00	0.98	0.00	0.96
60	0.00	0.98	0.00	0.96

[Phenol] = 24ppm, [H_2O_2] = 122ppm, Wool = variable, [Fe] = Variable, time = variable

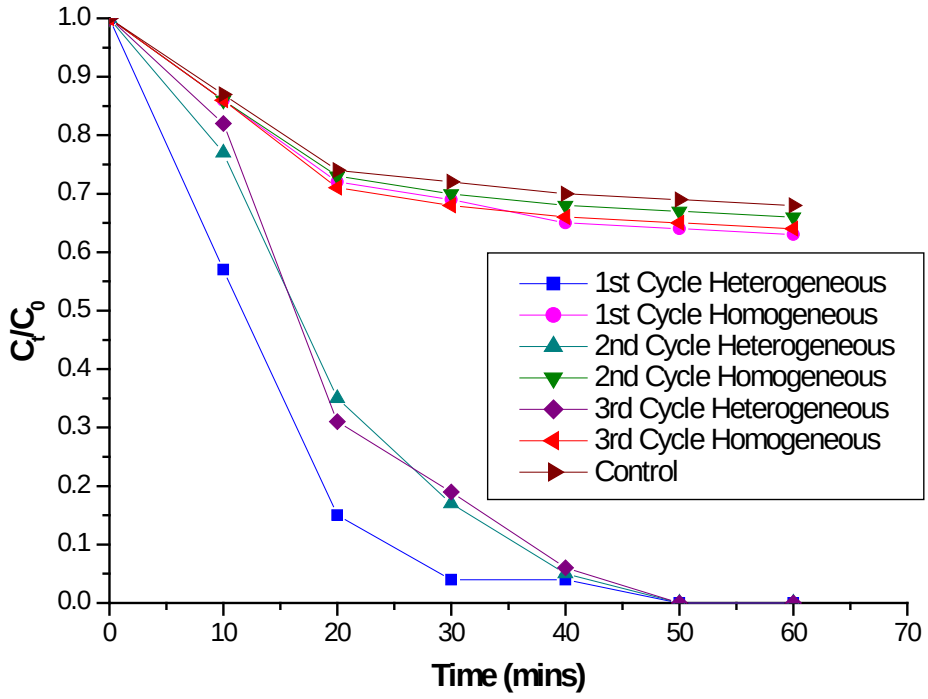


Figure 3.6 Heterogeneous and homogeneous catalysis results for the reduction in phenol (C_t/C_0) obtained using 1.0g wool catalyst

100% of phenol was decomposed by the catalyst over three cycles with between 2 and 6% homogeneous contribution. The cycle length was reduced to 50 minutes using 1.0g wool catalyst compared with ~98% decomposition in 60 minutes with 0.6g as achieved in previous studies (see section 3.4.1, Table 3.7).

3.5 Conclusions

3.5.1 Static batch evaluation of catalysis

Non-modified impregnated wool catalysts do not perform well. The batch-to-batch reproducibility is low regardless of wool type. Results indicate that iron fixation is lower as the homogeneous contribution to catalysis for unmodified wools was around 50% compared with less than 20% for modified and impregnated catalysts.

The hydroxylamine modified and impregnated wools demonstrate excellent batch-to-batch reproducibility for heterogeneous catalysis. There is generally low homogeneous contribution to catalysis. However, both Dark Grey Herdwick and Swaledale samples demonstrated high levels of homogeneous contribution to catalysis. It must be noted that the wools are coloured fleeces and in terms of dyeing such fleeces are treated differently to accommodate the affects of melanin. For example a mordant bleaching process is employed where an iron (II) salt in the presence of hypophosphorous acid (H_3PO_2) is applied, this is an iron reducing agent (ARIFOGLU and MARMER, 1991). Once this wool is rinsed iron (II) can be removed from the keratin but not from the melanin pigment granules (LEWIS, 1992). However, with the presence of H_2O_2 melanin granules can be destroyed by a free radical degradation process (Fe^{2+}/H_2O_2 is a powerful radical generation system).

When fibres containing iron (II) are immersed in H_2O_2 bleaching occurs at the pigment site. The presence of iron (II) ions in melanin leads to radical conversion and formulation of perhydroxy anions. Increasing the number of radicals close to the melanin causes a more complete disruption of melanin polymer by ring-opening reaction. The ring-opening step may lead to the higher level of homogeneous catalysis.

The melanin oxidation reaction is illustrated in Figure 3.7. Mordant-treated wools when used in dyeing are known to have problems with fastness (how strongly the dye is held on the wool).

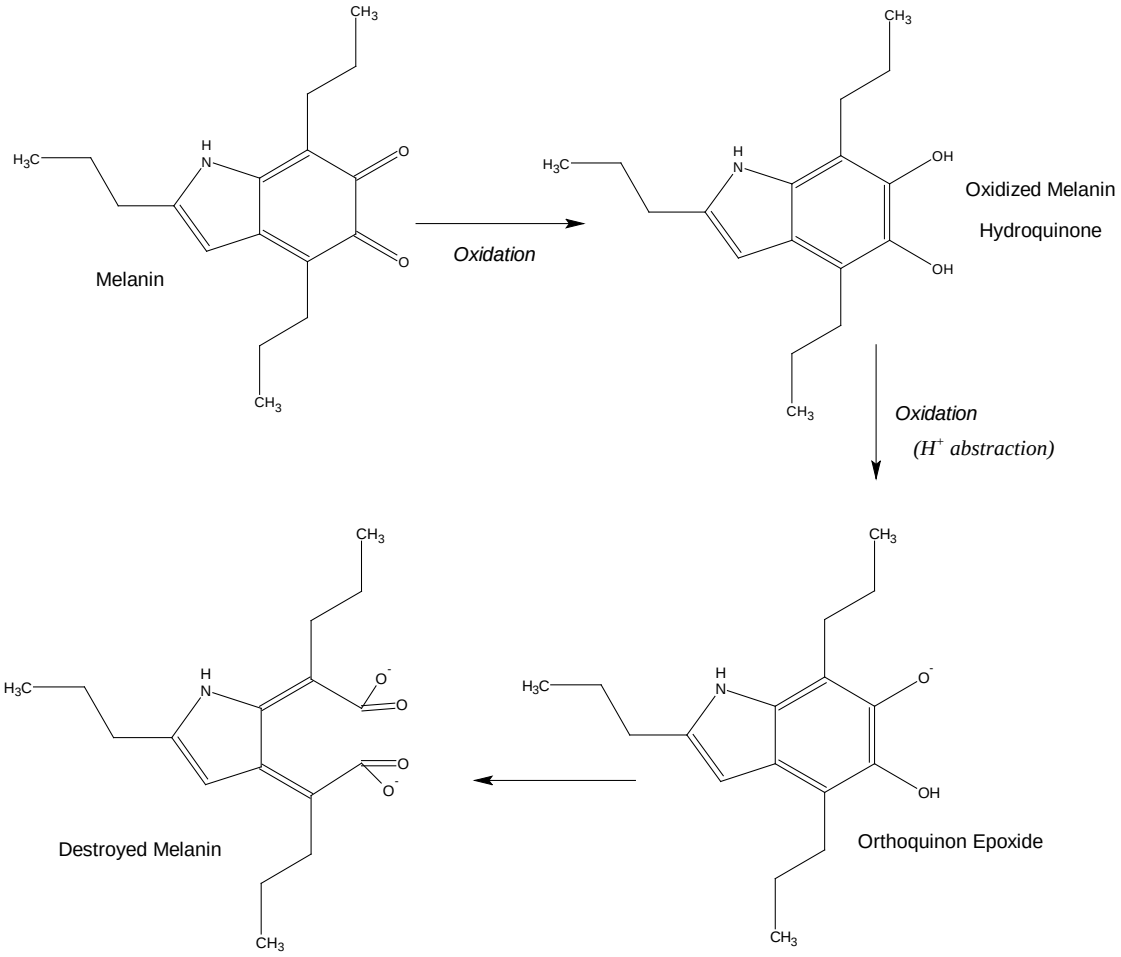


Figure 3.7 The Oxidation Reaction of Eumelanin (MONTAZER et al., 2009)

The costs of the wools provided by Thomas Chadwick and Sons Ltd are given in Table 3.17. Unfortunately the costs of the Woolmark and DEFRA samples are not known at this time, however, it is known that the Woolmark samples are the most expensive.

Table 3.17 2007 Prices for Thomas Chadwick Wools

Wool	Non-scoured (£/ kg)	Scoured (£/ kg)
Dark Grey Herdwick	£0.15-0.25	£0.50-0.70
Swaledale	£0.40-0.50	£0.90-1.10
Blackface	£0.80-0.95	£1.50-1.70
Crossbred	£0.90-1.00	£1.60-1.70
Halfbreds	£0.90-1.00	£1.80

Figure 3.8 provides a summary of the catalytic activity and homogeneous contribution of all seven wools evaluated for hydroxylamine modified and Fe (III) impregnated samples.

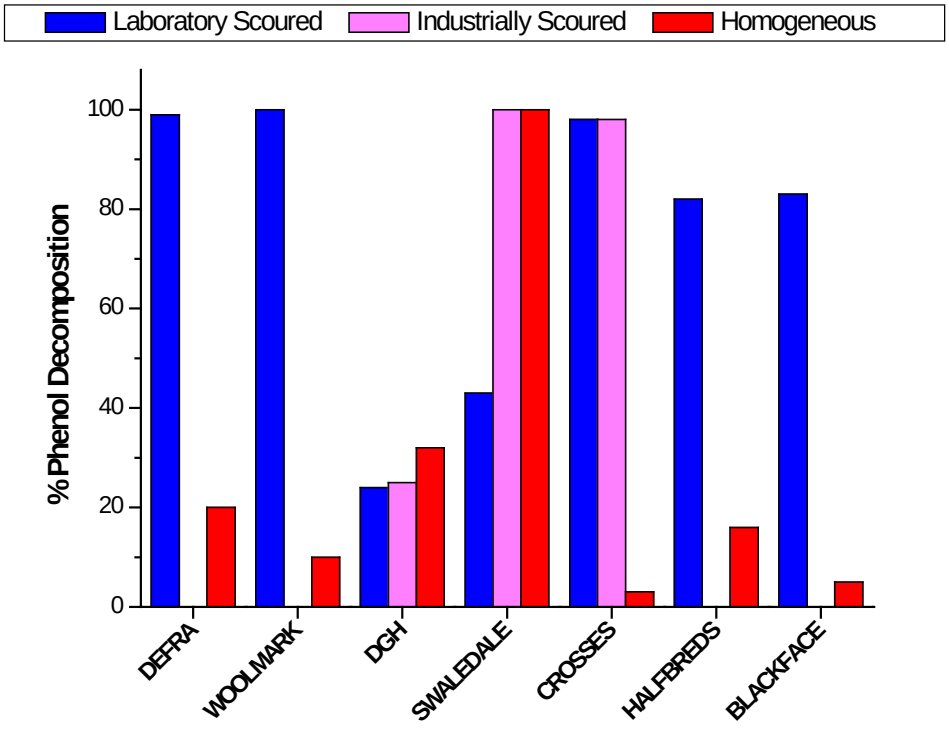


Figure 3.8 Seven Wool comparison for Laboratory Scoured (and Mill Scoured where applicable), Hydroxylamine modified and Fe (III) impregnated wools – 3rd Cycle of catalysis for phenol system, including homogeneous testing. [Phenol] = 24ppm, [H_2O_2] = 50ppm, Wool = 0.6g, [Fe] = Variable, time = 60 minutes

From Figure 3.8 and considering costs it can be seen that the wool to take forward and evaluate further is the Crossbred sample. Finally, based on the results obtained, it was decided mainly to test hydroxylamine and 50:50 hydrazine/hydroxylamine modified wools at pH 7 impregnated with Fe (III) at room temperature in the oxidative decomposition of phenol.

3.5.2 Catalyst longevity

In order to draw meaningful conclusions from the data collected in each dynamic study the following calculations were required,

- The yield degree of the substance (α),
- Mass of the substance decomposed (M)
- Turn-over frequency (TOF)

The yield degree of the substance (α) was calculated using the following equation:

$$\alpha = \frac{S}{\frac{C_t}{C_0} \times t}$$

- S = Area above the dynamic curve calculated by the total area minus the area below the curve obtained by integration using the computer program Origin (see Figure 3.9).
- $\frac{C_t}{C_0}$ = ratio between concentration of the substance in solution at time t (C_t) and initial concentration (C_0).
- t = duration of the process (min), for this example t = 2520 mins.

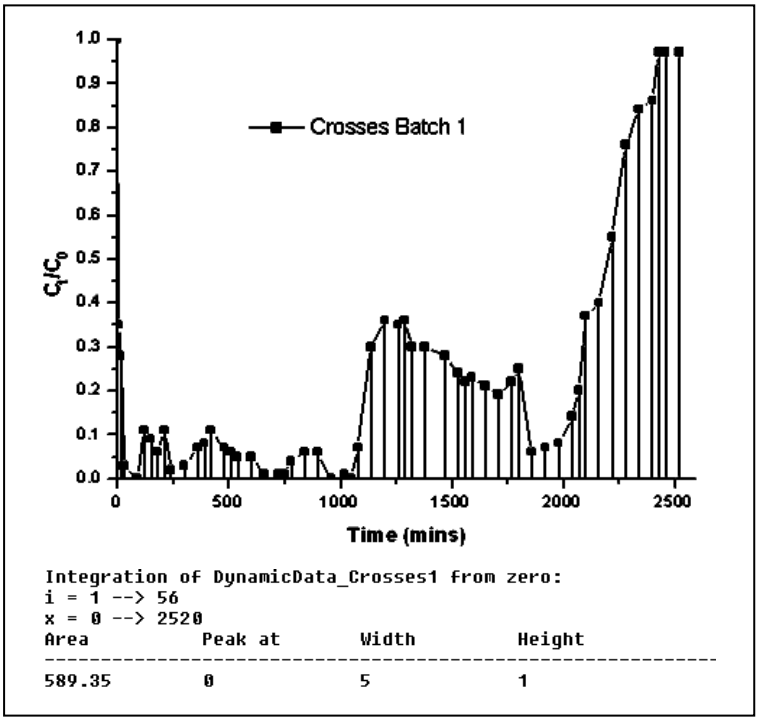


Figure 3.9 Crossbred dynamic study graph illustrating the integration using computer program origin

Total area is 2520 ($x_{\max} \times y_{\max}$) and the area below the curve obtained through integration is 589.35, therefore in this case S = 2520 – 589.35.

Mass of the substance decomposed (oxidized), M (mg), on the wool catalyst during the continuous process was calculated as follows:

$$M = \alpha \times Q \times t \times C_0$$

Q = flow rate (ml/min), which was 2 ml/min for all experiments.

In organometallic catalysis, the term turnover number is commonly used (TON). This relates to the number of moles of substrate that a mole of catalyst can covert before becoming deactivated. Taken further, the turnover per unit time is often given, known as the turnover frequency (TOF). For industrial applications, the TOF is in the range of 10^{-2} - 10^{2} s^{-1}. TOF is expressed as follows and in this case relates the amount of phenol decomposed to the active sites on wool:

$$TOF = \frac{Phenol}{[Fe] \times Wool \times t}$$

Phenol = amount of phenol decomposed (mmol), [Fe] = concentration of iron (mmol / g wool) and Wool = amount of wool support (g) which was 2g in all cases.

Table 3.18 displays the required input data for the calculations and α, M and TOF for each dynamic study are given in Table 3.19.

Table 3.18 – Data for each dynamic study required in order to calculate Turn-over Frequency

Sample	S	C_t (ppm)	C_0 (ppm)	$\frac{C_t}{C_0}$	t (mins)	Phenol (mmol)	Fe (mmol / g wool)
Crossbred (1)	1930.65	24.345	25.098	0.97	2520	1.0617	0.0738
Crossbred (2)	1960.30	24.117	25.122	0.96	2520	1.0950	0.0811
Crossbred (Fe^{3+}/Ca)	2489.15	25.000	25.771	0.97	2940	1.4055	0.0804
Crossbred (Fe^{3+}/Li) (1)	2968.15	25.015	25.526	0.98	3600	1.6422	0.0791
Crossbred (Fe^{3+}/Li) (2)	3020.23	25.124	25.637	0.98	3600	1.6788	0.0791
DEFRA	1879.73	24.493	25.514	0.96	2520	1.0616	0.0877
DGH	361.15	23.375	24.098	0.97	1470	0.0179	0.0543

Table 3.19 – Results corresponding to Turn-over Frequency for each dynamic study

Sample	α	M (mg)	TOF (min^{-1})
Crossbred (1)	0.790	99.930	2.8544×10^{-3}
Crossbred (2)	0.814	103.065	2.6789×10^{-3}
Crossbred (Fe^{3+}/Ca)	0.873	132.289	2.9730×10^{-3}
Crossbred (Fe^{3+}/Li) (1)	0.841	154.565	2.8835×10^{-3}
Crossbred (Fe^{3+}/Li) (2)	0.856	158.006	2.9477×10^{-3}
DEFRA	0.777	99.915	2.4018×10^{-3}
DGH	0.253	17.925	1.1927×10^{-3}

It was found that using the improved impregnation techniques did not result in additional Fe (III) loading, nor did it noticeably affect leaching. For all experiments excluding that of the Dark Grey Herdwick sample, no iron was detected in solution phase throughout catalysis. This suggests that phenol was not decomposed in solution by homogeneous catalysis, further confirmed when analyzing deactivated wool catalyst for iron content. On comparing these results with the original iron content the difference was minimal at ~ ± 3.0%. Therefore no iron had leached from wool samples. In the case of Dark Grey Herdwick, iron was found in solution throughout catalysis suggesting leaching of iron into solution. This was further confirmed by ~50% reduction in iron content on wool post catalysis.

DEFRA wool behaved in the same manner as the Crossbred wool when impregnated with Fe (III). Samples were found to have a loss of activity between 17 and 30 hours, followed by an increase in activity prior to complete deactivation. This phenomenon was not observed in samples prepared using the improved impregnation technique of Fe (III)/Ca or Fe (III)/Li. The catalyst lifetime was increased from 42 hours with the use of Fe^{3+}/Ca (49 hours) or Fe^{3+}/Li (60 hours) impregnation techniques. When using the improved impregnation technique, the turn-over frequency (TOF) was increased from ~2.7×10^{-3} to ~2.9×10^{-3} min^{-1}. The TOF values were very similar for both Fe^{3+}/Ca and Fe^{3+}/Li, however due to the increased lifetime, Fe^{3+}/Li was selected for replication

studies. Using the improved impregnation technique resulted in slightly higher TOF, suggesting that the rate of catalysis is slightly faster.

It was hoped that this study would identify the Dark Grey Herdwick wool as an efficient heterogeneous catalyst over a longer period of analysis. However, the turn-over frequency was very poor, 1.197×10^{-3} min^{-1}. At this stage it can be concluded that the Dark Grey Herdwick wool is not suitable for further analysis.

3.5.3 Optimisation of catalysis

The most efficient cycles were achieved when using 1.0g of wool catalyst. 100% phenol reduction was achieved after 50 minutes and was sustained over three cycles. The homogeneous contribution to catalysis was low at between 2% and 6%. At this time the increase in hydrogen peroxide does not seem to have affected the performance of the catalyst. All results were within the 5% experimental error limit. There was very good reproducibility between the two different runs. Future evaluations will now use 1.0g of catalyst.

Chapter 4 Catalyst Characterisation

4.1 Introduction

This work can be divided into two areas, the first area providing physical information relating to the catalyst and the second, chemical information of the wool fibre throughout treatment. Fibre diameter, tensile strength and extension analysis were carried out providing physical information. Tensile strength and extension studies provided relevant data of significant importance when relating back to longevity results. The fibre diameter study was to look for correlations between surface area, coarseness and catalytic activity. A study of fibre morphology using Scanning Electron Microscopy (SEM) followed by Energy Dispersive X-ray (EDX) was conducted to investigate the surface elemental composition for raw, scoured, modified and deactivated wool fibres was carried out. The study was used to confirm the iron distribution within the fibres and any visible surface changes that occurred throughout the processing. Infra-red analysis was also used to analyse the chemical composition of unmodified, modified and impregnated wools.

4.1.1 Physical characterisation

Scoured wool samples were subjected to fibre diameter analysis to investigate any correlation between catalyst performance and factors such as diameter, curvature and comfort factor. It was thought that the fibre diameter may have been a factor that influenced catalyst performance. A separate area of work was also to investigate the affects of modification, impregnation and catalysis on the wool fibre by evaluating the change in tensile strength and extension after each stage of processing. It was expected that the tensile strength would be reduced after modification, however it was not known what affect would be observed on further processing of the fibre.

4.1.2 Chemical characterisation

Fibre morphology was analysed using Scanning Electron Microscopy (SEM) followed by Energy Dispersive X-ray analysis, EDX, is a technique used to generate an x-ray spectrum from electron bombardment of the sample. As the bombarding electron collides with the samples' electrons, some are displaced. The position vacated is filled by an higher-energy electron from an outer shell. To do this, the transferring electron must give up some of its energy by the emission of an x-ray. The EDX spectrum is a plot of how frequently an x-ray is received from each energy level, allowing for elemental analysis. This technique was used to investigate the surface elemental composition for raw, scoured, modified and deactivated wool fibres. Select fibres were then subjected to further cross-sectional and longitudinal analysis to evaluate the dispersion of iron throughout fibres. A second area of this work was to investigate the chemical surface changes in wool after each stage of processing, scouring, modification, impregnation and catalysis. Wools had been prepared prior to this study by the methods previously outlined in Chapter 2. Standard FT-IR techniques would prove difficult as the fibres cannot be ground or dissolved as this would alter the chemical nature of the wool. This is especially significant when considering the environment in which iron is bound for impregnated fibres. Infrared Attenuated Total Reflectance (IR-ATR) was the technique chosen for this study as little or no sample preparation would be required.

Basic principles of infrared spectroscopy

Infrared spectroscopy is also known as vibrational spectroscopy as the resultant spectra arise from the difference between vibrational energy levels of a molecule. Infrared radiation occurs at wavelengths longer than visible light, 400nm-700nm, but shorter than microwaves, that is, shorter than 1mm. For chemical information, the mid-infrared region at wavelengths 2.5μm to 25μm, or more commonly, frequencies between 4000 and 400 wavenumbers, is most useful.

Infrared absorption results form a change in the vibrating state of a molecule. Vibrational energy levels are quantised, therefore only frequencies of radiation matching the harmonic vibrational frequencies of the sample molecule will be absorbed.

When IR radiation of appropriate energy is supplied to a molecule, energy can only be absorbed if the molecular vibration causes a change in the magnitude of the dipole moment of the molecule. Where there is a great magnitude of change in the dipole moment associated with a vibration, the more intense the absorption becomes. This is due to the transfer of the IR photon energy to the molecule being more efficient. The intensity of an infrared absorption band is proportional to the square of the change in the dipole moment.

The characteristic frequencies of a molecule are determined by the masses of the atoms and the strength of the bonds connecting them in the molecule. A higher frequency of vibration occurs with lower masses as the vibrating units (atoms or groups of atoms). In the presence of strong bonding a frequency of vibration occurs. For example, a triple bond has a higher vibrational frequency than a double bond provided the atoms have the same mass. Chemical environment influences vibrational frequency, resulting in inductive and mesomeric (resonance) effects. This causes a shift in the vibrational frequency due to a change in the electric distribution.

Diatomic molecules only have one mode of vibration involving the symmetric stretching of the bond between the two atoms. In polyatomic molecules there are a wide number of vibrations which involve the atoms in the molecule or a specific group of atoms within it. These include, symmetric and asymmetric stretching of bonds and the rocking, wagging, scissoring and twisting of bond deformations. The IR spectrum of a complex polyatomic molecule is likely to contain a large number of vibrations, some of which will be associated with vibrations of individual bonds or functional groups, while others must be considered as vibrations of the whole molecule. The latter are often referred to as “fingerprint” bands due to their unique position, intensity and number. They usually fall in the region below $1500cm^{-1}$.

Quantitative infrared analysis is based on the Beer-Lambert Law. This suggests that the absorbance is proportional to the concentration of corresponding species. In many cases, scattered radiation makes the direct application of Beer-Lambert law inaccurate. Generally, quantitative analysis is carried out by measuring the absorbance of a specific

band relative to another unrelated band in the spectrum, or by using an internal standard of known concentration.

Attenuated Total Reflectance (ATR) spectroscopy

The technique of Attenuated Total Reflectance combats the challenging aspects of infrared analysis, namely sample preparation and spectral reproducibility. An ATR accessory operates by measuring changes occurring in a totally internally reflected beam as the beam makes contact with the sample as demonstrated in Figure 4.1 an infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. The resultant internal reflectance creates an evanescent wave extending beyond the crystal surface into the sample held in contact with the crystal. Evanescent waves are formed when the waves travelling in a particular medium undergo total internal reflectance at the boundary due to the waves striking the boundary at an angle greater than the critical-angle. This evanescent wave has a penetration depth of 0.5-5 μ; therefore there must be sufficient contact between the sample and crystal. In the infrared regions where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each wave is passed back to the IR beam which then exits at the other end of the crystal to the detector in the IR spectrometer allowing an infrared spectrum to be generated. In order to obtain good results using IR-ATR technique the following conditions are required.

- Samples must be in direct contact with the ATR crystal as the evanescent wave only extends beyond the crystal 0.5-5 μ.
- The refractive index of the crystal must be significantly greater than that of the sample or the internal reflectance will not occur – light will be transmitted rather than internally reflected within the crystal. In general, ATR crystals have refractive index values between 2.38 and 4.01 at 2000cm^{-1}. It can be assumed that most liquids and solids have much lower refractive indices.

Thallium bromide/iodide (KRS-5), zinc selenide and germanium are typical ATR crystal materials.

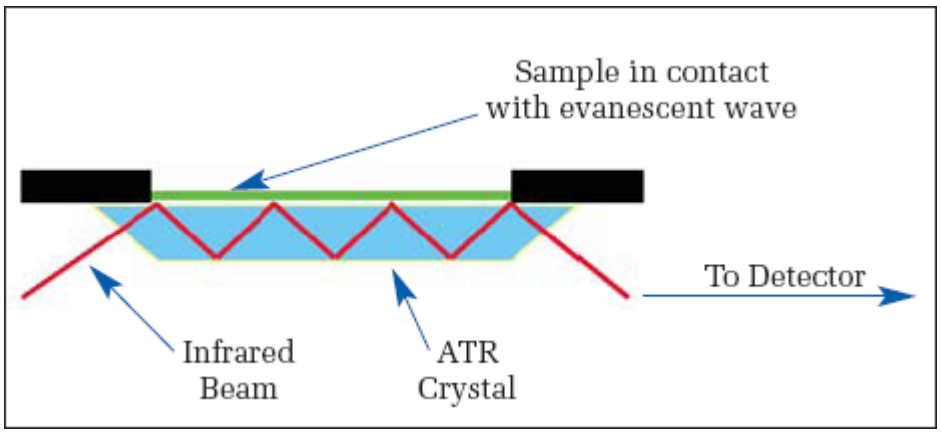


Figure 4.1 A multiple reflection ATR system

4.2 Materials and Chemicals

The wool samples analysed for fibre diameter and infra-red studies are listed in Table 4.1 and Table 4.2.

Table 4.1 Samples for fibre diameter analysis including supplier and chemical processing applied.

Wool	Supplier	Chemical Processing
WOOLMARK	WOOLMARK	As provided by WOOLMARK
DEFRA	FERA	Laboratory Scoured at DMU (see Section 2.3.2)
Dark Grey Herdwick	Thomas Chadwick & Sons	Industrially Scoured
Swaledale	Thomas Chadwick & Sons	Industrially Scoured
Crossbred	Thomas Chadwick & Sons	Industrially Scoured
Halfbreds	Thomas Chadwick & Sons	Industrially Scoured
Blackface	Thomas Chadwick & Sons	Industrially Scoured
Crossbred	Thomas Chadwick & Sons	Industrially Scoured, hydroxylamine modified & impregnation Fe (III) (see Sections 2.3.3 and 2.3.4)

Table 4.2 Samples for Infra-red analysis including supplier and chemical processing applied.

Wool	Supplier	Chemical Processing at DMU
Mill Scoured Crossbred	Thomas Chadwick & Sons	N/A
	Thomas Chadwick & Sons	Hydroxylamine Modification
	Thomas Chadwick & Sons	Hydroxylamine Modification & Impregnation (Fe^{3+})
	Thomas Chadwick & Sons	Hydroxylamine Modification & Impregnation (Fe^{3+}/Ca)
	Thomas Chadwick & Sons	Hydroxylamine Modification, Fe^{3+}/Ca & dynamic catalysis with phenol
Non Scoured Top Wool	FERA	N/A
	FERA	Non-scoured & Impregnated (Fe^{3+})
	FERA	Non-scoured, Impregnated (Fe^{3+}) & static phenol catalysis
	FERA	Laboratory non-ionic scouring
	FERA	Laboratory scouring & Impregnation (Fe^{3+})
	FERA	Laboratory scouring, Impregnation (Fe^{3+}) & static phenol catalysis
	FERA	Laboratory scouring & 50:50 Modification
	FERA	Laboratory scouring, 50:50 Modification & Impregnation (Fe^{3+})
	FERA	Laboratory scouring, 50:50 Modification, Impregnation (Fe^{3+}) & static phenol catalysis
	FERA	Laboratory Scouring & Hydroxylamine Modification
	FERA	Laboratory Scouring, Hydroxylamine modification & impregnation (Fe^{3+})
	FERA	Laboratory Scouring, Hydroxylamine modification, Fe^{3+} & static phenol catalysis

Where identified, samples had been treated using the methods previously outlined in Chapter 2 and Chapter 3.

4.3 Methods

4.3.1 Fibre Diameter Measurements

Scoured wool samples were analysed to determine their Mean Fibre Diameter (MFD), also known as fibre fineness. The IWTO-12 test specification was used (International Wool Textile Organisation, 2009). This is the measurement of the mean and distribution of fibre diameter using the Laserscan fibre diameter analyser. Short lengths of the fibre (known as snippets, 0.8-2mm long) were cut from individual fibres at random positions along the length of the fibres. This was done using a mini-core, an instrument used alongside the Laserscan to ensure continuity when cutting fibre lengths. The snippets were then dispersed into an iso-propanol / water mixture and the resultant suspension allowed to flow through the measurement cell. The Laserscan used had been calibrated at regular intervals using wool tops where the Mean Fibre Diameter (MFD) and diameter distribution has been previously determined by direct measurement using a Projection Microscope. Appendix 4 includes a schematic diagram of the Laserscan.

MFD is defined as the average diameter of a sample of fibres in μm. For wool, the mean diameter is weighted for length as individual fibres have differing lengths. The Laserscan evaluates the mid-point and performs the following calculation – Equation 33.

$$MFD = \frac{\sum n \times d}{\sum n} \qquad \textbf{Equation 33}$$

Where, n = the number of snippets and d = diameter at the mid-point (μm).

The Standard Deviation (SD) is a measure of the dispersion of individual results. It is calculated by the Laserscan using Equation 34,

$$SD = \sqrt{\frac{\sum n \times d^2 - \frac{\left(\sum n \times d\right)^2}{\sum n}}{\sum n - 1}}$$ **Equation 34**

Coefficient of Variation of Fibre Diameter (CVD) is defined as a statistical measurement of the variability exhibited within a set of values, expressed as a percentage of the mean. Therefore a high CVD indicates a greater variability. The following Equation 35 is used by the Laserscan to calculate the CVD.

$$CVD = \frac{SD}{MFD} \times 100$$ **Equation 35**

The Laserscan uses the following, Equation 36 to produce the curvature values,

$$Curvature = \frac{1}{R}$$ **Equation 36**

R is defined as the radius of the arc of the fibre. Curvature is expressed as degrees per millimetre. Samples were analysed for a total of 5000 snippets.

4.3.2 Tensile strength and Extension at Breaking

Samples were sent to WOOLMARK Testing laboratory for testing. The method used was BS EN ISO 5079:1995 Determination of breaking force and elongation at break of individual fibres. Fifty fibres were measured for each sample investigated and the test gauge length was 20mm. The Crossbred samples evaluated were as follows

- Industrially scoured
- Industrially scoured and hydroxylamine modified
- Industrially scoured, hydroxylamine modified and impregnated Fe (III)
- Industrially scoured, hydroxylamine modified, impregnated Fe (III) post deactivation

4.3.3 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis of wool

Strands of fibre were carefully placed on a carbon stub so that that they did not overlap and that there were not too many fibres as this would cause the fibres to stand up away from the stub resulting in charging. The edge of the stub was trimmed before gold plating for a period of one minute. All samples had been kept in a desiccator to prevent moisture uptake by the fibres. Post coating, samples were again returned to the controlled atmosphere prior to analysis. All samples were prepared in this way.

Each sample was subjected to the same microscope conditions. These were as follows:
Accelerating Voltage = 10 kV; Beam Current = 150 pA;
Filament Current = 2.08 A; Working Distance = 15 mm.

For EDX analysis the following adjustment to the microscope conditions were required: Beam Current = 3500 pA; Working Distance = 19 mm.

Cross and longitudinal sections of DEFRA wool fibres for EDX analysis were prepared in accordance with technique described by Ishtchenko et al (2003a).

4.3.4 IR-ATR

Perkin Elmer Spectrum One Instrument - provided by De Montfort University and Leicester University. Their specifications are given in Table 4.3

Table 4.3 Perkin Elmer Spectrum One Instrument Specifications

University	Serial Number	Optics	ATR Crystal	IR Region used (cm^{-1})
De Montfort	73953	KBr	ZnSe	500-4000
Leicester	67852	CsI	ZnSe	250-500

Each sample was analysed in duplicate for bulk samples (many fibres) and dilute samples (2 or 3 fibres). The conditions used are given below in Table 4.4.

Table 4.4 Infrared conditions applied to the samples analysed

IR Region evaluated (cm^{-1})	Force Applied to Sample (N)	Number of Scans Performed
250-500	100	8
500-4000	100	8

4.4 Results and Discussion

4.4.1 Physical Characterisation

Fibre Diameter Results and Calculations

The Diameter Distribution Histograms obtained for each sample are given in Appendix 5 to Appendix 11 and are used to calculate the comfort factor (CF) by evaluating the percentage of fibres finer than 30μm. A summary of the data obtained is given in Table 4.5 and comparison histograms for scoured Crossbreds and DEFRA wools are given in Figure 4.2.

Table 4.5 Fibre Diameter Analysis Data

Wool Sample	MFD (μm)	SD (μm)	CVD (%)	Curvature (deg/mm)	CF (%)
WOOLMARK	23.5	5.0	21.3	75.0	91.8
DEFRA	40.3	6.5	16.1	70.2	5.0
D. G. H	34.3	12.6	36.8	74.1	44.3
Swaledale	31.3	12.4	39.5	81.2	57.3
Mill scoured Crossbred	34.1	9.5	27.9	70.3	37.7
Halfbreds	34.5	8.2	23.8	86.2	33.2
Blackface	36.8	13.2	35.9	66.0	36.4

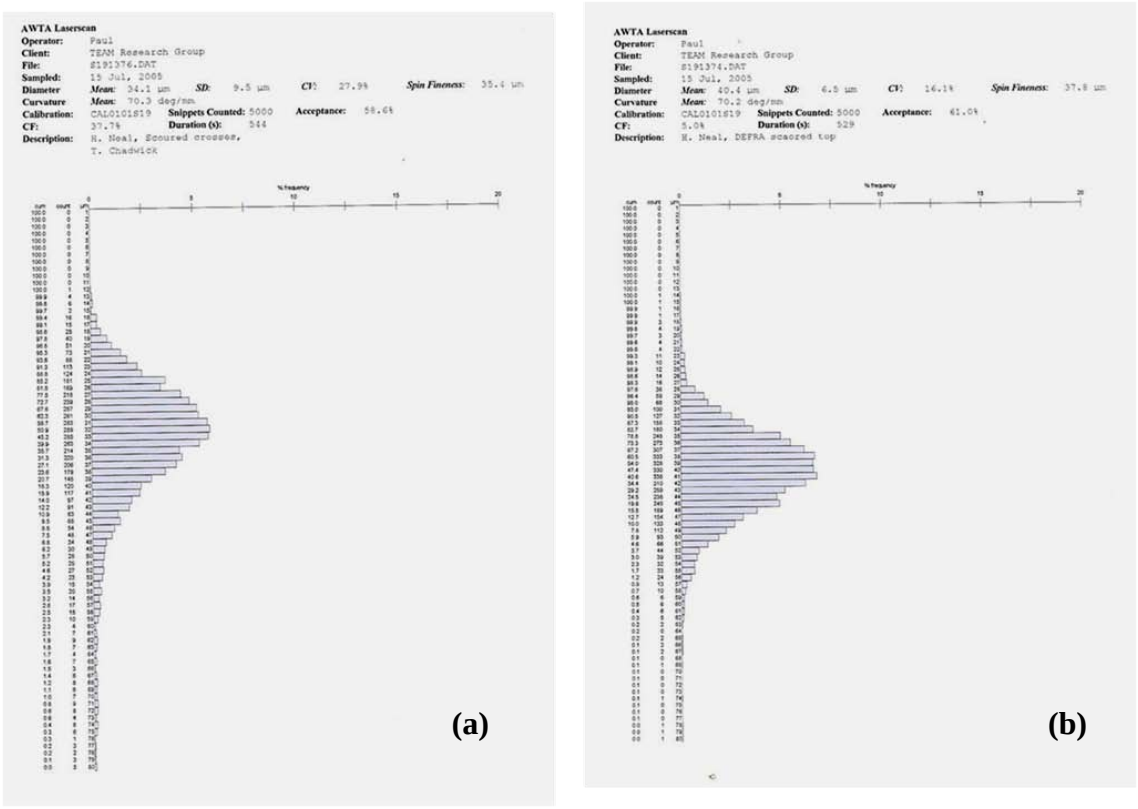


Figure 4.2 Laserscan Histograms obtained for scoured (a) Crossbreds and (b) DEFRA wools.

From the results it can be seen that there is no obvious connection between fibre diameter and catalytic performance of the final modified and iron impregnated fibre. Fibre diameter can be related to both stiffness and surface area, therefore it was considered that a finer fibre would be easier to penetrate. However this hypothesis has not been confirmed with the catalytic activity results obtained.

The catalytic behaviour of both WOOLMARK and Crossbred are similar, yet their mean fibre diameters are 23.5µm and 34.1µm, respectively. Furthermore the Swaledale wool performs badly with a high level of homogeneous contribution to catalysis but has a mean fibre diameter of 31.3µm. It was found that the DEFRA top wool was the thickest with a diameter of 40.3µm. The remaining wools had diameters between 31 and 37µm. This would suggest that the catalytic performance of the wool fibres (post modification) is independent of fibre diameter. All other data obtained using the Laserscan shows no clear trends.

4.4.1.1 Tensile strength and Extension at Breaking

Crossbred wool samples after each stage of treatment were evaluated for their tensile strength and extension at breaking. The findings are given in Table 4.6 and Figure 4.3.

Table 4.6 Results for the BS EN ISO Determination of breaking force and elongation at break of individual Crossbred fibres

Tensile Property	Crossbred Wool			
	Scoured	Modified	Impregnated	Deactivated
Breaking Load (g)	23.8	15.8	14.1	13.1
Extension (%)	45.6	18.6	20.1	30.6

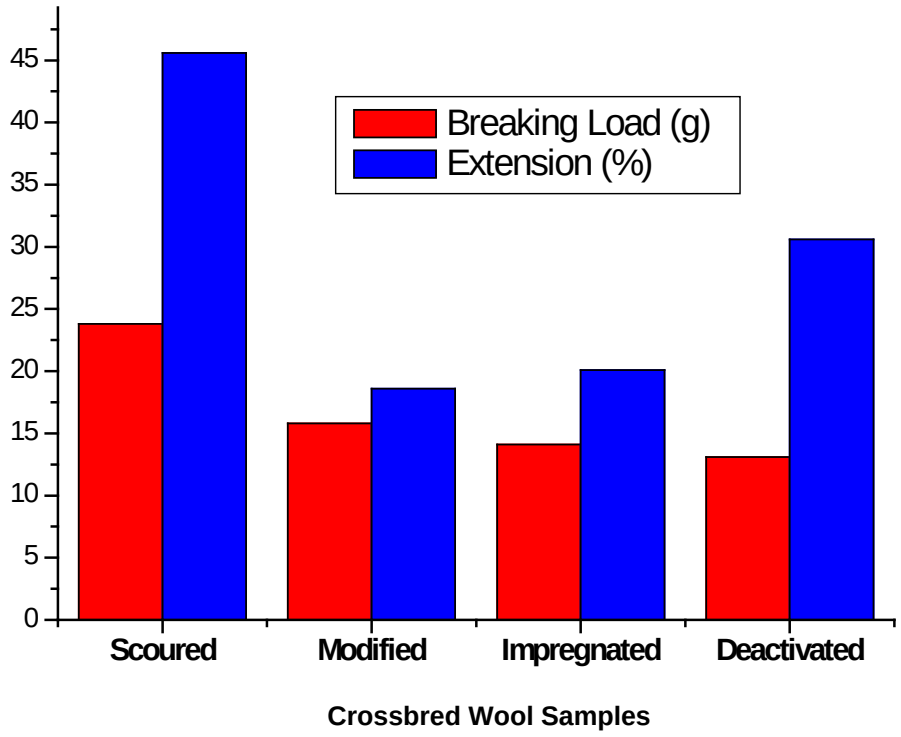


Figure 4.3 Graphical representation of the results obtained in the BS EN ISO Determination of breaking force and elongation at break of individual fibres

As expected the most significant loss in tensile strength was observed after modification (~34.5% reduction). The treatment involved in modifying the fibres is the most intensive of the processing carried out, even when adjusting to pH 7. On comparing deactivated fibres with modified fibres there is only a 17% loss in tensile strength at deactivation which is comparatively small when considering the loss of ~34.5% from modification alone. As the fibres are being loaded they are undergoing axial tensile deformation. As with many α-helix formations, the fibres undergo a three phase deformation, firstly small-deformation as the wool fibre is stretched homogeneously, secondly the helical structure begins to break with the rupture of H-bonds and finally, large-deformation of the fibre following covalent bond stretching. The loading required to go through the three phases will be dependent on the treatment performed on the wool fibres, as demonstrated by the results discussed. Prior to modification the fibres are quite stretchy as confirmed by the extension results, however the results suggest that fibres become more brittle after modification. It was also shown that after an initial reduction in extension, some of this has been regained throughout the processing. The modified and impregnated wool can still withstand the length of catalysis treatment (42 hours) as described previously in Section 3.4.2.

4.4.2 Chemical Characterisation

4.4.2.1 SEM and EDX analysis of wool

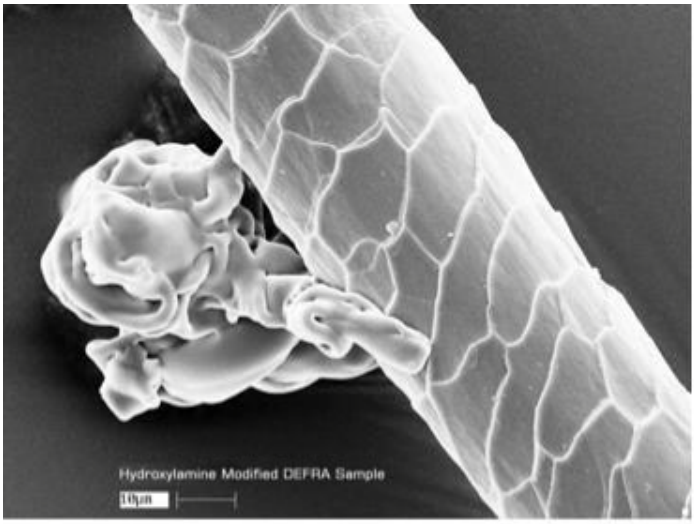
Scanning Electron Microscopy (SEM) was used to investigate whether the surface of wool had been damaged by any of the processes used in this study to prepare a catalyst. Table 4.7 document any significant findings for the SEM/EDX study of the wool catalysts prepared from DEFRA top wool in the forms of raw, scoured, modified and modified & Fe (III) impregnated samples.

Table 4.7 Significant results arising from the SEM/EDX study on DEFRA wool samples

Sample	SEM/EDX Comments
Non-scoured wool	Grease, wax and dark spots can be clearly identified. No definition in the cortical cells. EDX identified the presence of S (due to the chemical composition of the wool) and K, thought to be present as an impurity.
Non-scoured and Fe(III) impregnated wool	Dark spots were no longer present and the greasy texture not as obvious. EDX showed little evidence of Fe (III) and shows Cl present, arising from impregnation with acidic $FeCl_3.6H_20$ and resulting from an ionic association between protonated amine groups on the wool or protonated carboxyl groups on grease and Cl^-.
Non-scoured, Fe(III) impregnated wool post phenol catalysis	No obvious change in fibre surface. Comparative analysis of the elemental composition showed the presence of Cl which is likely to have arisen from the impregnation of wool fibre with acidic $FeCl_3.6H_20$. Traces Al found on wool post catalysis, an impurity from the gold plating.
Scoured wool	The image clearly showed that the greasy and waxy effect found in the non-scoured sample had been removed. Cortical cells were well defined.
Scoured and Fe(III) impregnated wool	Laboratory scoured wool was impregnated with a solution of acidic $FeCl_3$, confirmed Fe presence with EDX results. No obvious surface changes.
Scoured, Fe(III) impregnated wool post phenol catalysis	Similar to image obtained for the Fe^{3+} non-scoured wool after catalysis. There was no obvious change to the fibre surface. Traces of Al were found which could be an impurity after gold plating procedure.
Scoured 50:50 hydrazine/hydroxylamine modified wool	After modification with a 50: 50 mixture image showed some changes in the fibre surface. Outer layers began to lift (peeling effect). It did not appear from the image to be affecting deeper layers.
Scoured 50:50 modified and Fe(III) impregnated wool	No obvious lifting of the cortical cells which remained well defined, giving the fibre a smooth appearance. Fe was clearly identified on the fibre through EDX analysis.
Scoured 50:50 modified, Fe(III) impregnated post phenol catalysis	No obvious damage to the fibre and cortical cells remain defined. Fibre's appearance was smooth with very little debris in the sample.
Scoured Hydroxylamine modified wool	Modification with hydroxylamine appeared to produce attachments on the wool, illustrated with the image in Figure 4.4. Structure could result from chemical peeling of the top surface of the fibre. The cuticle structure still present. F found to be present, most likely arisen from instrumental error. Occasionally EDX analysis provides limited sensitivity between elements.
Scoured Hydroxylamine modified and Fe(III) impregnated wool	Sample appeared to have greater level of debris. Unidentified structures attached to the fibre as before. Image of the fibre was similar to the example provided in Figure 4.4. In some cases, attachments provide a link between fibres. Possible that modification is producing a cross-linking affect between fibres.
Scoured Hydroxylamine modified, Fe(III) impregnated wool post phenol catalysis	Branching structures were observed. Little peeling was on the actual fibre. EDX identified Cu present, most likely from the preparation of the sample such as gold plating.

SEM/EDX analysis of cross- and longitudinal-sections of DEFRA wool fibres

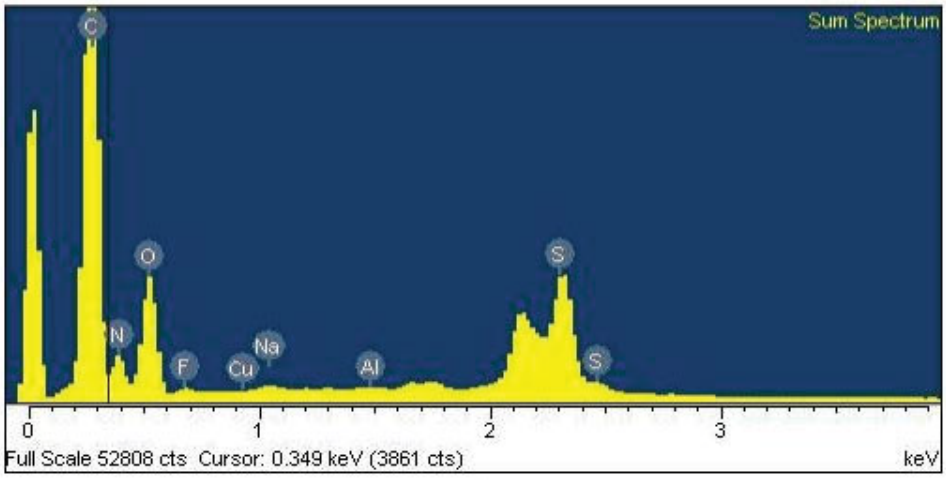
EDX analysis was used to determine the depth of penetration of iron (III), as well as, the presence of other elements, such as oxygen, sulphur and chlorine, within the fibre by examination of cross and longitudinal sections. Modified and Fe (III) impregnated DEFRA top wool fibres before and after phenol catalysis were examined. The results are shown in Figure 4.4 to Figure 4.7. In all cases the images are representative of the whole sample. The branching was also observed in the hydroxylamine modified Crossbreds sample as demonstrated in Figure 4.5.



(a)

Element	Weight%	Atomic%
C	50.82	56.95
N	22.39	21.51
O	23.89	20.09
F	0.80	0.57
Na	0.11	0.06
Al	0.03	0.01
S	1.85	0.78
Cu	0.10	0.02
Totals	100.00	

(b)



(c)

Figure 4.4 SEM/EDX Analysis of DEFRA Scoured & Hydroxylamine Modified Wool. (a) SEM Image (b) EDX Element Quantification (c) EDX Spectrum

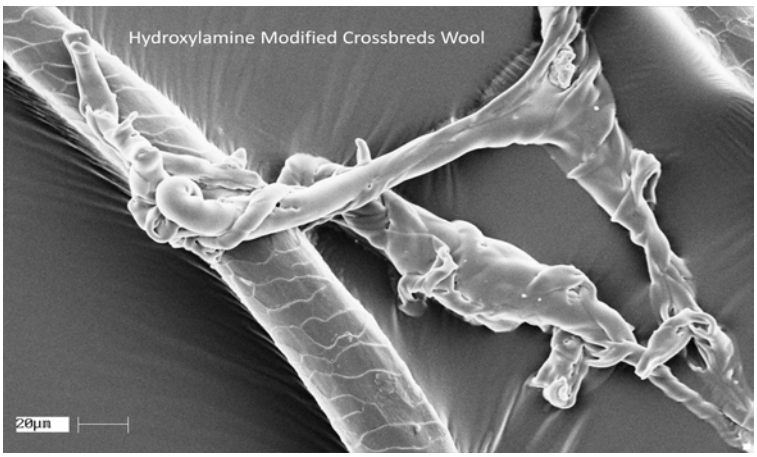


Figure 4.5 SEM image of the hydroxylamine modified crossbreds wool demonstrating branching.

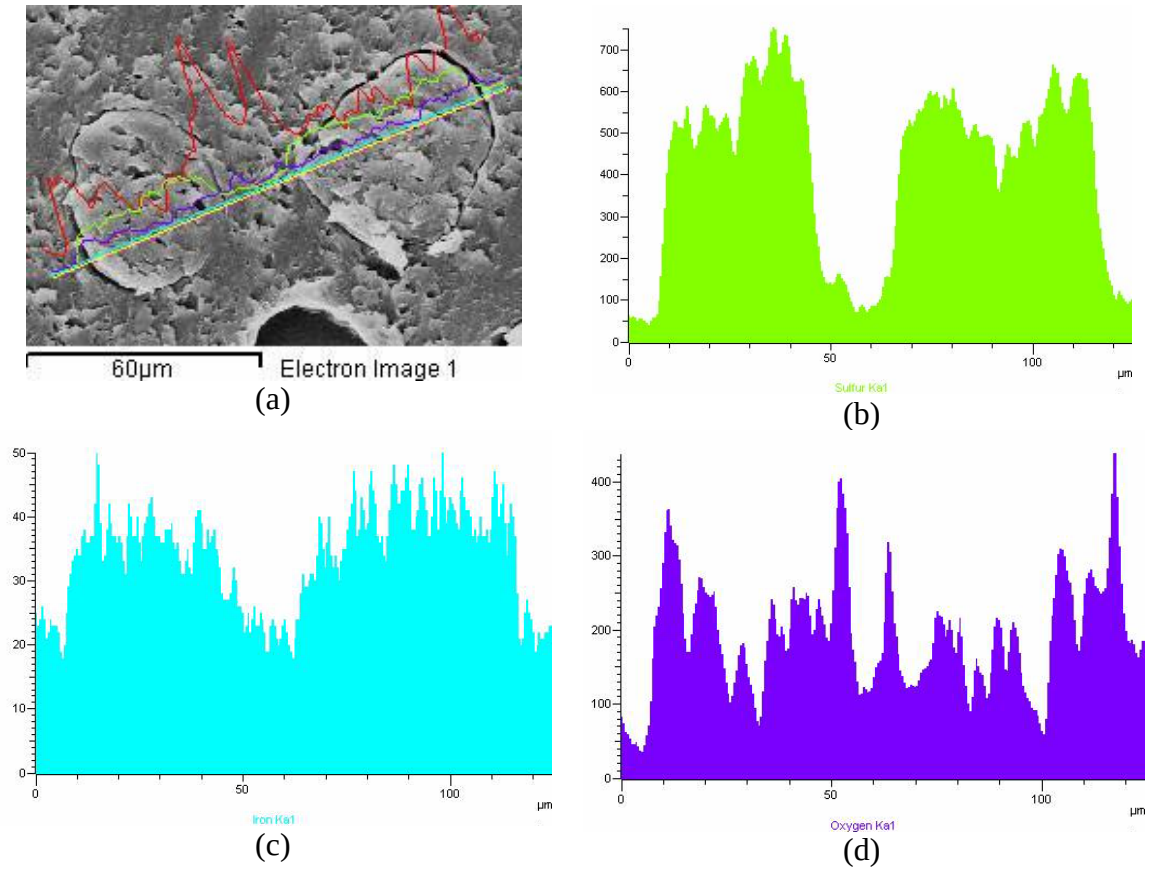


Figure 4.6 SEM/EDX analysis of cross section of Scoured, Hydroxylamine Modified & Fe (III) Impregnated DEFRA Wool. (a) SEM image; (b) EDX of sulphur; (c) EDX of iron and (d) EDX of oxygen, along cross section of the fibre.

* Red spectrum in (a) represents carbon distribution along cross section of the fibre, which solely derives from the carbon sample holder and does not make any contribution to the chemical composition of wool fibre sample.

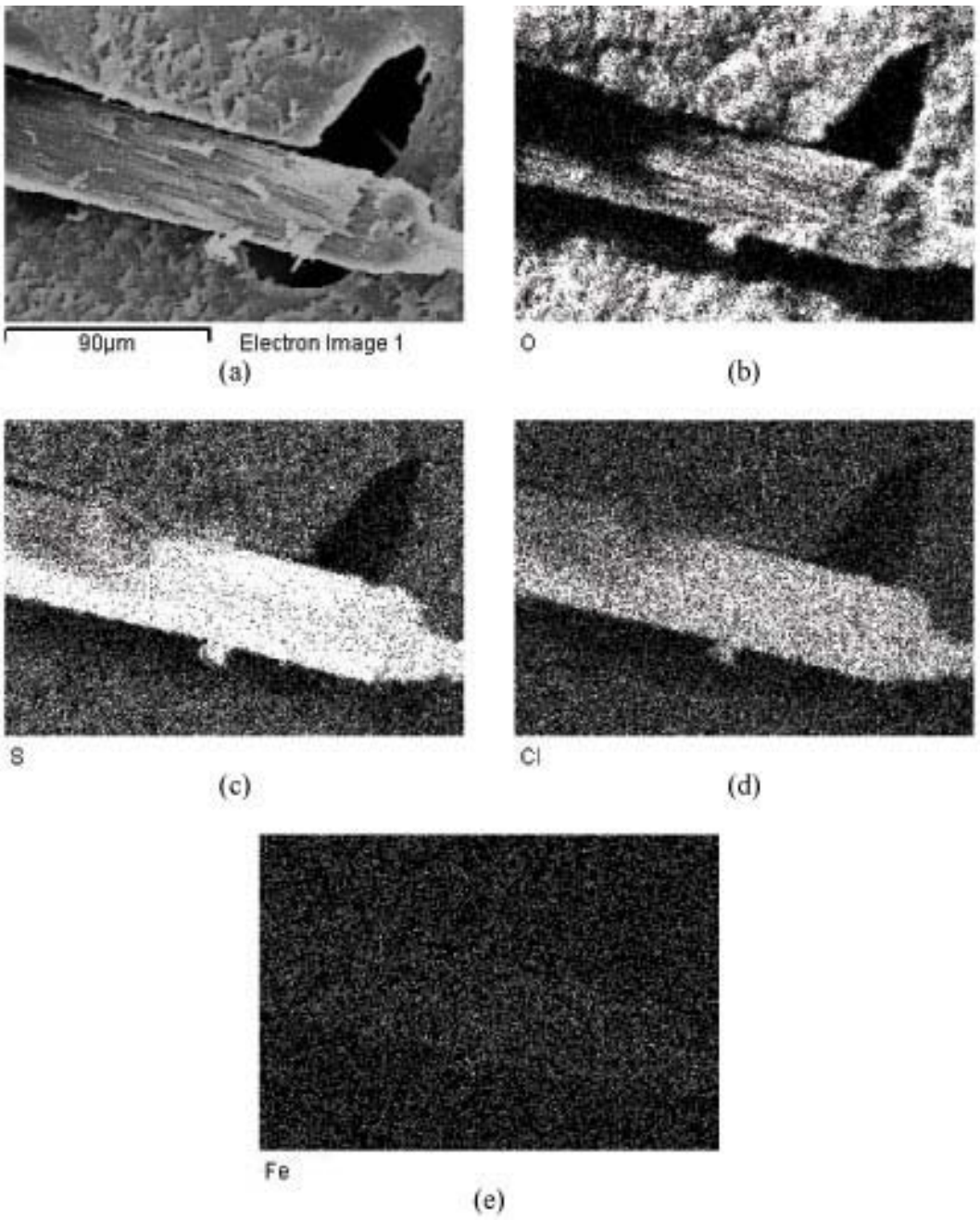


Figure 4.7 SEM/EDX analysis of longitudinal section of Scoured, Hydroxylamine Modified & Fe (III) Impregnated DEFRA Wool. **(a) SEM image; EDX mapping of (b) oxygen, (c) sulphur, (d) chlorine and (e) iron, along longitudinal section of the fibre.**

It was found that for both cross and longitudinal sections of modified and Fe (III) impregnated DEFRA top wool fibres, iron, sulphur and chlorine were present on the external surfaces and throughout the interior of the wool fibre. In particular, iron and chlorine penetrate deeply into the interior of the wool fibre during impregnation stage

with ferric chloride solution. Sulphur, being a major constituent of wool, was found extensively on the fibre identified by EDX mapping of sulphur (Figure 4.6 c) which is very pronounced in comparison to the other elements. There were no significant changes with respect to EDX analysis of the wool fibres after phenol catalysis.

4.4.2.2 Infra-red Results

The FT-IR (ATR) transmittance spectrum after each stage of processing for DEFRA wool are shown in Figure 4.8 and for Crossbred wool are displayed in Figure 4.9. This first set of results corresponds to the frequency range, 500cm^{-1} - 4000cm^{-1}. Table 4.8 lists the main band assignments for this region.

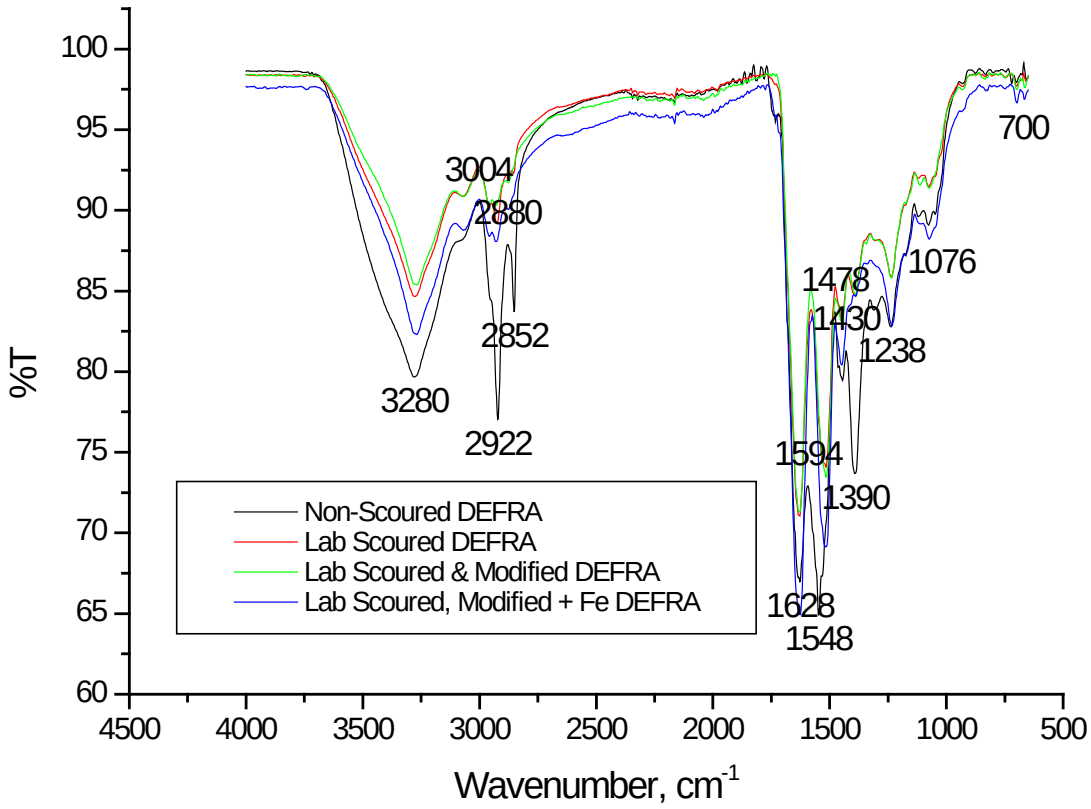


Figure 4.8 – IR-ATR spectrum of DEFRA wool after each stage of processing (500cm^{-1}-4000cm^{-1}), modification regime was hydroxylamine.

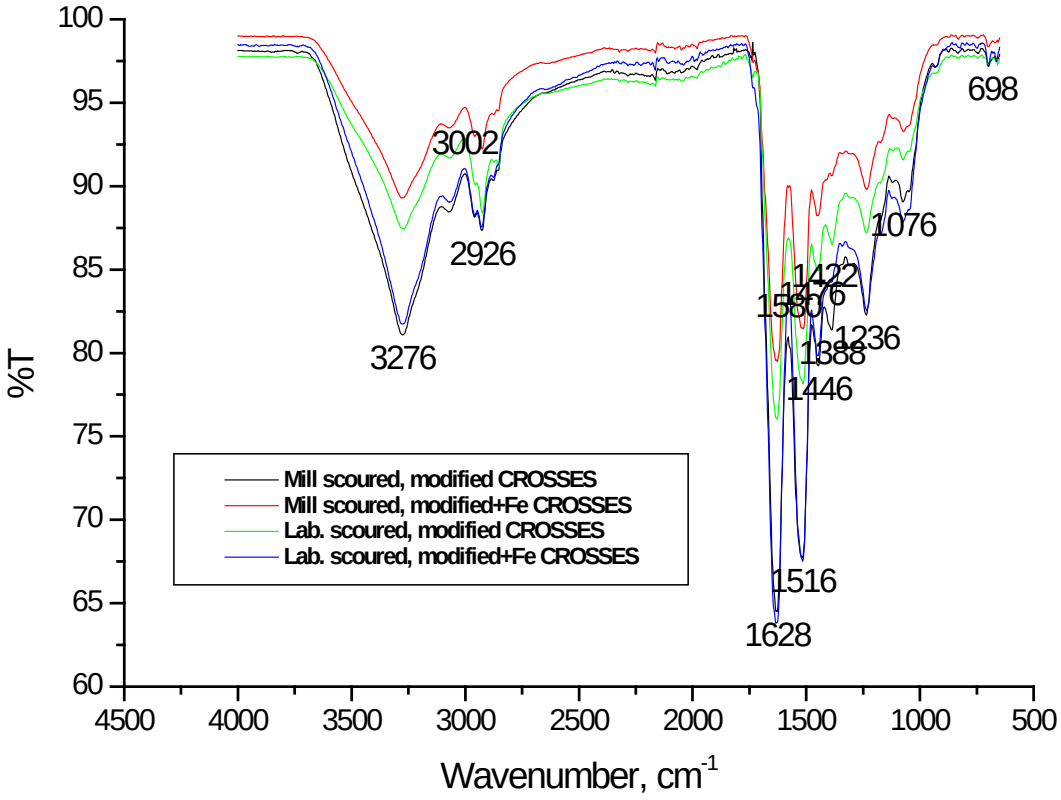


Figure 4.9 IR-ATR spectrum for Crossbred wool after each stage of treatment (500cm^{-1}-4000 cm^{-1}), modification regime was hydroxylamine.

Table 4.8 – Infrared band assignments for wool (500cm^{-1} – 4000cm^{-1})

Frequency (cm^{-1})	Assignment
~3278	N-H (s) Secondary amides O-H (s) hydrogen bonded (broad)
~3003	Amide II overtone
~2924	CH_3 (as)
~2852	CH_2 (ss)
~1628	Amide I, C=O (s), C-N (s), C-C-B (d)
~1530	Amide II, N-H (ib), C-N (s), C-C (s)
~1426	CH_2 and CH_3, C-H (d)
~1389	CH_3, C-H (d)
~1237	Amide III, N-H (ib), C-N (s)
~1076	$-C_2H_5$, $-C_3H_7$
~699	N-H (d)

(s) stretch (ss) symmetric stretch (as) asymmetric stretch (ib) in plane bond (d) deformation

Figure 4.8 and Figure 4.9 showed that CH_3 groups at 2922cm^{-1} and 1390cm^{-1} are removed on scouring. These probably arise due to long chain fatty acids. The main change observed in the spectra is after scouring as described above, there is little change on modification or impregnation which can be seen here.

As can be seen from the IR-ATR results above, no significant changes in wool were observed as a result of treatment in the frequency range 500cm^{-1} – 4000cm^{-1}. In all cases samples were analysed in duplicate to check for reproducibility and the spectra given are representative of all samples.

4.5 Conclusions

There is no obvious connection between fibre diameter and catalytic performance of the fibre. The catalytic behaviour of both WOOLMARK and Crossbred are similar, yet their mean fibre diameters are 23.5μm and 34.1μm, respectively. Furthermore the Swaledale wool performs badly with a high level of homogeneous contribution but has a mean fibre diameter of 31.3μm. It was found that the DEFRA top wool was the thickest with a diameter of 40.3μm. The remaining wools had diameters between 31 and 37μm. All other data obtained using the Laserscan shows no clear trends.

As previously mentioned, the most significant loss in tensile strength was observed after modification. This was expected as the chemicals used for modification are strong with the wool being exposed to them at 100-101^{o}C for an extended period of time. The treatment involved in modifying the fibres is the most intensive even when adjusting to pH 7. Fortunately there is little loss in strength due to catalysis as identified when comparing results after impregnation with those after deactivation. After an initial reduction in extension, it was observed that some extension was regained throughout the processing. This may be due hydration of the fibres as all stages are in the presence of water.

It was seen from the SEM images in Figure 4.4 that the cuticle structure was present and was representative of all samples analysed. For the fibres modified with hydroxylamine

only or 50:50 hydrazine/hydroxylamine mixture some minor changes on the surface of cuticle scale occur, not affecting other deeper layers. Thus, cells forming the outer layer (cuticle) have begun to lift (peeling effect) after modification of the wool fibre with 50:50 hydrazine/hydroxylamine mixture. This effect was more pronounced (formation of the branching structures) when fibre had been modified with hydroxylamine only. The presence of Fe and Cl was shown by EDX analysis on wool fibres, impregnated with ferric chloride solution.

For both cross and longitudinal sections of DEFRA top wool fibre, iron, sulphur and chlorine were present on both the external surfaces and the interior of the wool fibre with no significant changes with respect to EDX analysis of the wool fibres after phenol catalysis. Unfortunately no significant changes in wool were observed using IR-ATR as a result of treatment in the frequency range $500cm^{-1}$ – $4000cm^{-1}$. On considering the cross-sectional results obtained from SEM/EDX work, iron can be clearly detected throughout the fibre. Thus, impregnation is not limited to the surface which may also indicate that is also the case for modification. IR-ATR is a surface analysis technique and therefore it is feasible that the surface concentration of that which is of interest may not be sufficient for this technique.

Chapter 5 Products of Catalysis

5.1 Introduction

The purpose of this study was to evaluate the products formed during the catalysis of Phenol. There has been much research carried out relating to the wet oxidation of phenol (BREMNER et al., 2006, SANTOS et al., 2002, SANTOS et al., 2005, TRYBA et al., 2006). Bremner et al., (2006) investigated the degradation of phenol with hydroxyl radicals and found that the optimum conditions utilise the continuous presence of iron metal, acidic pH and concentrated hydrogen peroxide. Tryba et al., investigated the kinetics of phenol decomposition under UV irradiation with and without hydrogen peroxide. They found that the phenol decomposition was accelerated under UV irradiation, brought about by the conversion to highly hydrophilic products and catechol. In all cases the reaction pathways illustrated in Section 1.4, Figure 1.24 (p 66) have been identified as possible routes of phenol decomposition. Santos et al. (Santos et al., 2002, Santos et al., 2005) identified and quantified phenol and organic intermediates by HPLC. Investigations have been carried out using a novel ion chromatography technique for the rapid identification and quantification of saturated and unsaturated low molecular weight organic acids formed during the Fenton oxidation of organic pollutants such as nonylphenol (CHI and HUDDERSMAN, 2007). During this investigation the acids determined were acetic, formic, propionic, butyric, oxalic, malonic, succinic, glutaric, adipic, acrylic and maleic acid. It was found that the quantification of both oxalic and maleic acid was difficult as they are lost in the solvent front. The conditions used in the study of nonylphenol have been replicated for the study with phenol as many of the organic acids produced are the same.

Unfortunately, ion chromatography cannot be used to detect aromatic ring products, hence the need to develop an alternative method. Literature suggests the use of HPLC to investigate compounds such as hydroquinone, benzoquinone and catechol. Quintanilla et al reported that such compounds could be determined by HPLC using a C-18 column with UV detection at 210 and 246nm (Santos et al., 2002). The mobile

phase used was 4mM sulphuric aqueous solution and acetonitrile (9:1 $^{v}/_{v}$) at a flow rate of 1 mL min^{-1}. Similar work has also been carried out by Santos et al. using the same column and mobile phase (SANTOS et al., 2005). In this investigation they adopted the use of gradient elution from 1 to 1.9 mL min^{-1} with the UV detection at 192, 210 and 244nm. Other studies have been carried out using alternate mobile phases, such as 1.85% phosphoric acid (99/1 $^{v}/_{v}$) (Tryba et al., 2006) and methanol/water (20-40% methanol) (BREMNER et al., 2006, CHI and HUDDERSMAN, 2007). The flow rate in these cases was 1 mL min^{-1}, however the UV detection ranged from 210-290nm.

Initial investigations will use the C-18 column and mobile phase which has been implemented in the analysis of phenol for previous catalytic investigations. The UV detection wavelength will require investigation in order to find the optimum for benzoquinone and catechol. It has been deemed very difficult to evaluate hydroquinone as it is highly reactive and unstable. However, it can be safely assumed that the presence of benzoquinone will confirm the presence of hydroquinone throughout the reaction. Once a suitable methodology had been developed the evolution of ring products during the early stages of catalysis was investigated.

A secondary objective of this study was to evaluate the degree of mineralisation of phenol throughout static batch studies. This was done effectively by measuring the total organic carbon (TOC) in the solution at various stages of catalysis. The following experiments were conducted;

1. Water acidified
2. Phenol acidified
3. Phenol, hydrogen peroxide and water, acidified with bubbled air
4. Hydrogen peroxide and water, acidified with bubbled air and wool catalyst
5. Phenol, hydrogen peroxide and water, acidified with bubbled air and catalyst

Typically TOC has been used as part of the online monitoring of wastewater quality (BOURGEOIS, W. et al., 2001). An advantage of this is that it is recognised as a global

parameter (SCOTT, J. P. et al., 1995). Chandler et al. (1976) found that due to limitations of bio-chemical oxygen demand (BOD) and chemical oxygen demand (COD) determinations, that TOC measurements were becoming an essential water quality parameter. It was found to be a useful tool allowing for more efficient sample collection, storage and analysis.

5.2 Materials and Chemicals

Wool fibre:

Industrially scoured Crossbred wool, supplied by Thomas Chadwick modified with hydroxylamine and Fe (III) impregnated was prepared using the methods previously outlined in Chapter 2 and subjected to phenol catalysis as described in Chapter 3.

Chemicals:

Table 5.1 Chemicals used and their respective supplier

Chemical	Supplier
Acetic Acid	Fisher Scientific Ltd., Loughborough, UK
Benzoquinone	Sigma-Aldrich, UK
Catechol	Sigma-Aldrich, UK
CC-Muconic Acid	Aldrich-Chemie GmbH, Steinheim, Germany
Formic Acid	Fisher Scientific Ltd., Loughborough, UK
Hydrochloric Acid	Sigma-Aldrich, UK
Malonic Acid	Aldrich-Chemie GmbH, Steinheim, Germany, and Sigma-Aldrich, Dorset, UK
Oxalic Acid	BDH Chemicals Ltd., UK
Potassium Hydrogen Phthalate	Sigma-Aldrich, UK
Succinic Acid	Sigma-Aldrich, UK

5.3 Methods

5.3.1 Ion Chromatography

Static catalysis cycles with the iron impregnated wool (1.0g), phenol (50mL, 24ppm), hydrogen peroxide (122ppm) and air were conducted. Initially, after 60 minutes samples were analysed using the Ion Chromatography (IC) method identified below for qualitative analysis. Once the technique had been established, samples were taken at more regular intervals throughout catalysis (15, 30, 45, 60 and 120 minutes) to confirm the reaction pathway suggested in literature.

The determination of organic acids was performed using the Metrohm Modular MIC-2 advanced system. Chromatograms were analysed using the Metrohm IC-Net 2.3 software. The system was run in isocratic mode with the column temperature at 30^{o}C. The ion exclusion technique with inverse suppression was used to separate the organic acids. Samples were injected via a 20µl loop and eluted at a flow rate of 0.5mL/min and 2.1MPa of pressure through a Metrosep 6.1005.200 organic acid analytical column (250mm x 7.8mm, particle size of 10µl, with polystyrene/divinyl benzene copolymer packing material). 0.38mM sulphuric acid was used as eluent. The suppressor system was regenerated by 100mM LiCl solution pumped through the suppressor unit simultaneously with double distilled water. Conductivity detector operated in the positive mode at a full scale of 1.0µS.

5.3.2 HPLC Method for the determination of Benzoquinone and Catechol

The optimum wavelength detection was determined by preparing a solution of the compound of interest and exposing it to a UV scan on a UV/VIS spectrophotometer. This produced a map of the absorptions, the strongest of which can then be used for detection with HPLC. The HPLC column was a standard C-18 (250 x 4.6mm) packed column with a mobile phase comprising of 40% $^{v}/_{v}$ methanol and 60% $^{v}/_{v}$ double distilled water at a flow rate of 1 mL/min. Sample volumes to be injected were 20µl. The compounds under investigation were benzoquinone and catechol. Standard solutions (10ppm) of each compound were prepared and analysed multiple times in order to confirm a stable retention time for each compound and reproducible peak area.

The UV detector was set to the respective λ_{max} identified from Figure 5.3 and Figure 5.4. Samples were analysed in triplicate.

5.3.3 Degree of mineralisation

The instrumentation employed was the Analytical Science Thermalox instrument version 2.5-manual injection. The instrument was composed of a total carbon (TC) reactor carrying the Platinum coated catalyst and quartz wool loosely packed to about 10 mm, embedded in an oven. The carrier gas was oxygen. Carbon dioxide produced was analysed using a Non-Diffusive Infra-Red (NDIR) gas analyser. The instrumental parameters were as follows:

- Carrier gas flow rate: 180 mL/min
- Oven temperature: 680 ^{o}C
- Target CV %: 4

Number of repeats if CV was not achieved: 2

A calibration of Total Organic Carbon (TOC) was performed using dilutions of potassium hydrogen phthalate (KPH) with acidified water (containing 0.1% HCl). Solutions were sparged with oxygen for 3 minutes in order to displace any dissolved CO_2. 30µl of each standard dilution was injected into the reactor and the TC and Total Inorganic Carbon (TIC) recorded allowing TOC to be calculated. Seven injections of each standard solution were required and the mean of the five best correlation measures considered. Samples collected from the static catalysis reactor outlet were prepared and analysed in the same manner.

The concentration of phenol used in all experiments was 24ppm. All solutions were acidified to ~pH 3.

For catalysis, the wool catalyst (1.0g) was placed in a dreschel bottle containing a solution (50mL) of phenol (24ppm) and hydrogen peroxide (122ppm). The vessel was sealed and bubbled air passed through. Samples were extracted every 15 minutes for a total of 60 minutes and analysed for TOC as previously described. A control run was

completed using the fresh feed prepared and analysed in the same manner; however, the catalyst was not included. This would provide the TOC data for the reaction between phenol and hydrogen peroxide. Finally, it was desirable to evaluate the effect of hydrogen peroxide on the wool catalyst. This was performed using wool (1.0g) placed in a solution of hydrogen peroxide (50mL, 122ppm). Samples were extracted every 15 minutes for 60 minutes and analysed for TOC as before. All experiments were duplicated for reproducibility.

5.4 Results and Discussion

5.4.1 Ion Chromatography data

Six organic acids were evaluated to confirm their appearance and disappearance throughout catalysis. The corresponding calibration equations for each of the six organic acids are given in Table 5.2. This information was then used in the initial qualitative analysis of the products formed during catalysis. An example of the chromatograph obtained can be found in Figure 5.1. At this early stage, only one peak was unidentified (peak 4 in Figure 5.1) at ~9.70 minutes.

Table 5.2 Organic acids with their purity, supplier, concentration range and retention times

Compound	Dissociation Constants (25°C)		Purity (%)	Supplier	Retention Time (min)	Calibration Equation
	pK_a	pK_{a2}				
Oxalic acid	1.23	4.19	99.5	BDH Chemicals Ltd., UK	6.85	y = 372.10x – 485.14
Malonic acid	2.83	5.69	99	Aldrich-Chemie GmbH, Steinheim, Germany, and Sigma-Aldrich, Dorset, UK	8.00	y = 382.37 – 62.66
Succinic acid	4.16	5.61	99	Sigma-Aldrich, UK	11.87	y = 1107.20 – 1651.60
Formic acid	3.75		99	Fisher Scientific Ltd., Loughborough, UK	12.05	y = 69.23x + 161.29
Acetic acid	4.76		99	Fisher Scientific Ltd., Loughborough, UK	14.63	y = 295.87x + 34.33
CC-Muconic acid	3.03	4.82	98	Aldrich-Chemie GmbH, Steinheim, Germany	19.36	Y = 0.71x + 6.72

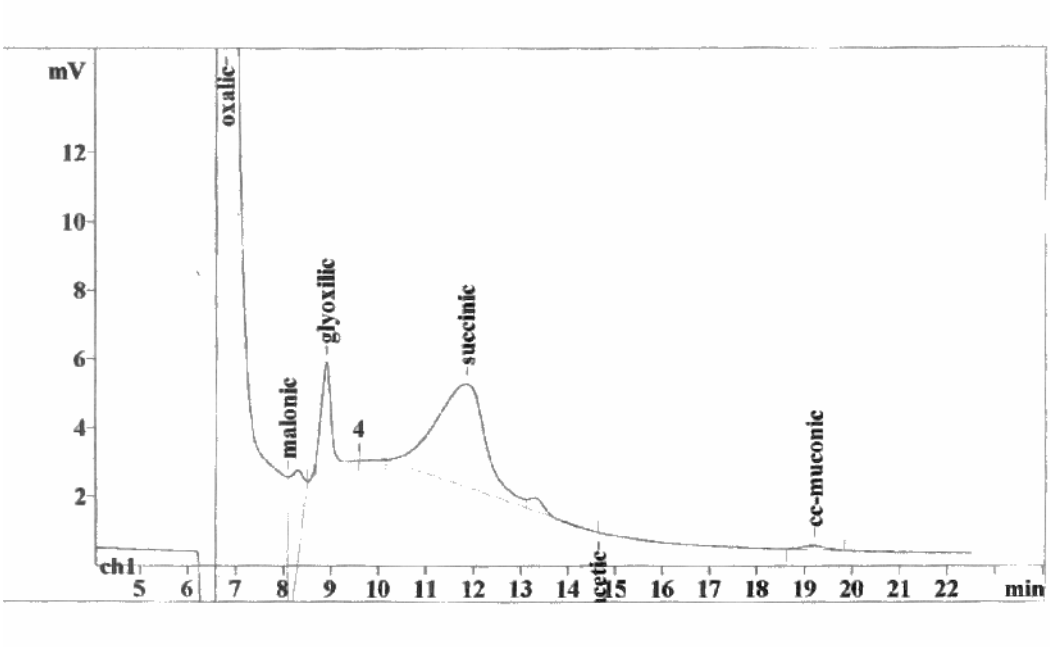


Figure 5.1 Ion chromatography results after 60 minutes of catalysis

Further quantitative analysis was carried out to investigate the evolution of organic acid products throughout catalysis (Table 5.3).

Table 5.3 Evolution of organic acid products from catalysis

Organic Acid	Retention Time (min)	R^2 Value	Run 1 (ppm)				
			15 Mins	30 mins	45 mins	60 mins	120 mins
Oxalic	6.85	0.9987	13.00	14.02	8.56	11.38	11.86
Malonic	8.00	0.9929	39.39	0.00	0.00	0.00	0.00
Succinic	11.87	0.9816	0.00	0.00	0.00	1.30	0.00
Formic	12.05	0.9901	0.00	295.31	21.35	0.00	0.76
Acetic	14.63	0.9999	0.00	0.00	0.00	0.00	0.08
CC-Muconic	19.36	0.9606	0.00	0.00	0.16	3.75	10.83

The evolution of these products is shown graphically in Figure 5.2.

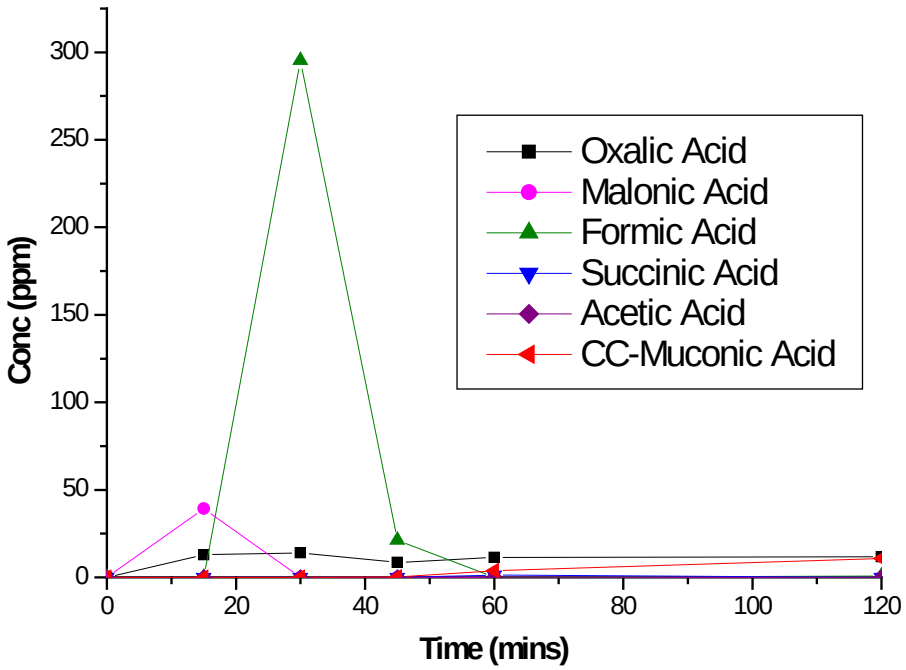


Figure 5.2 Evolution of products of catalysis after 120 minutes

Results indicated very good reproducibility between runs. Results obtained relating to oxalic acid will require further investigation as it elutes at a very similar time to chlorine which is present in the reaction solution. Quantification of oxalic acid would ideally be performed with LC-MS to enable it to be distinguished from the presence of chlorine resulting from impregnation and pH adjustment of the feed. It is also possible that maleic acid is present but again may be disguised as the chlorine peak occurring at ~7 minutes.

5.4.2 Ring product methodology

Samples of known concentrations of catechol and benzoquinone were evaluated for their maximum absorptions in order to develop a methodology for ring-product quantification during catalysis. Figure 5.3 showed that the maximum absorption was achieved at λ_{max} = 237.0nm for catechol. This would give the best peak resolution when using HPLC with UV/Vis detection. Figure 5.4 shows that the maximum absorption for

benzoquinone was achieved at λ_{max} = 200.5nm. These conditions could now be implemented in a HPLC detection method for catechol and benzoquinone.

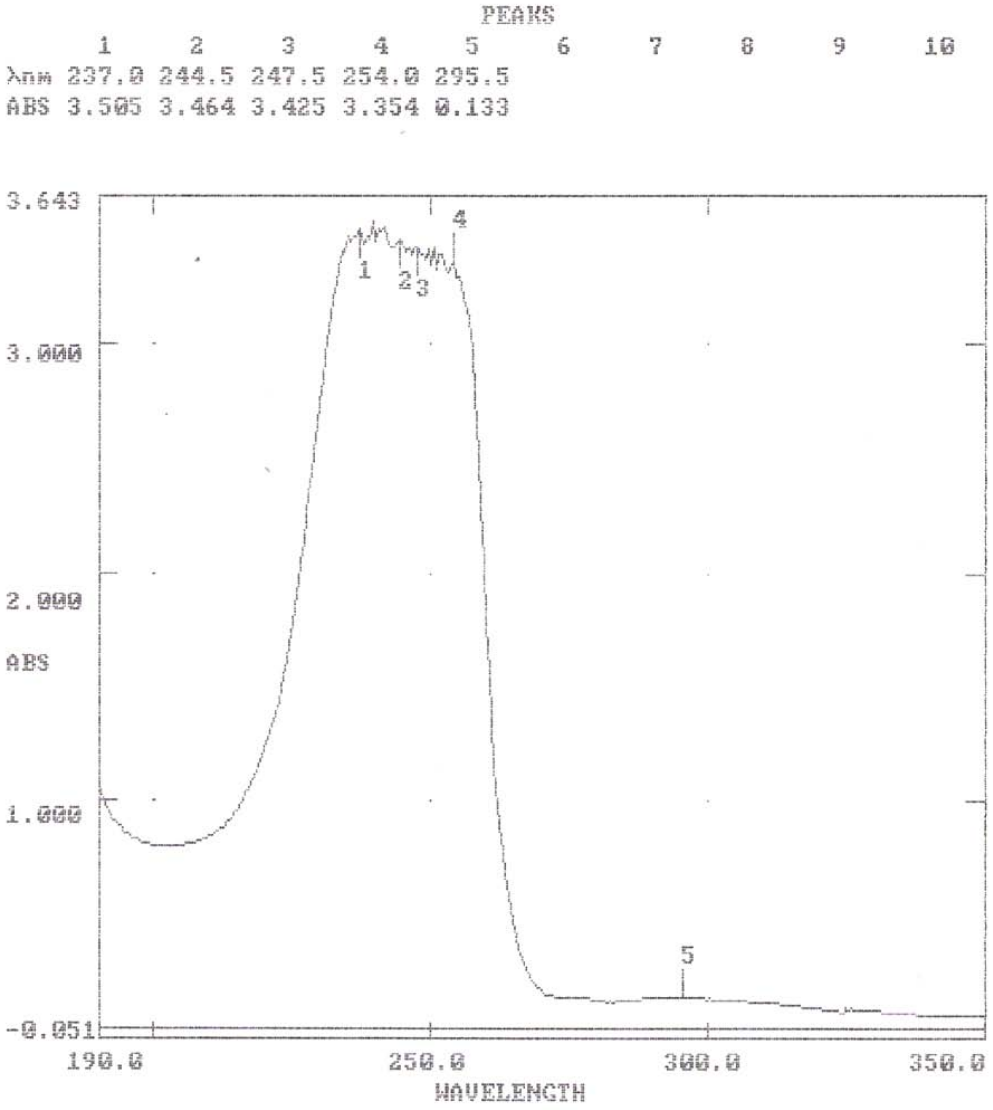


Figure 5.3 UV/Vis absorptions for Catechol dissolved in water

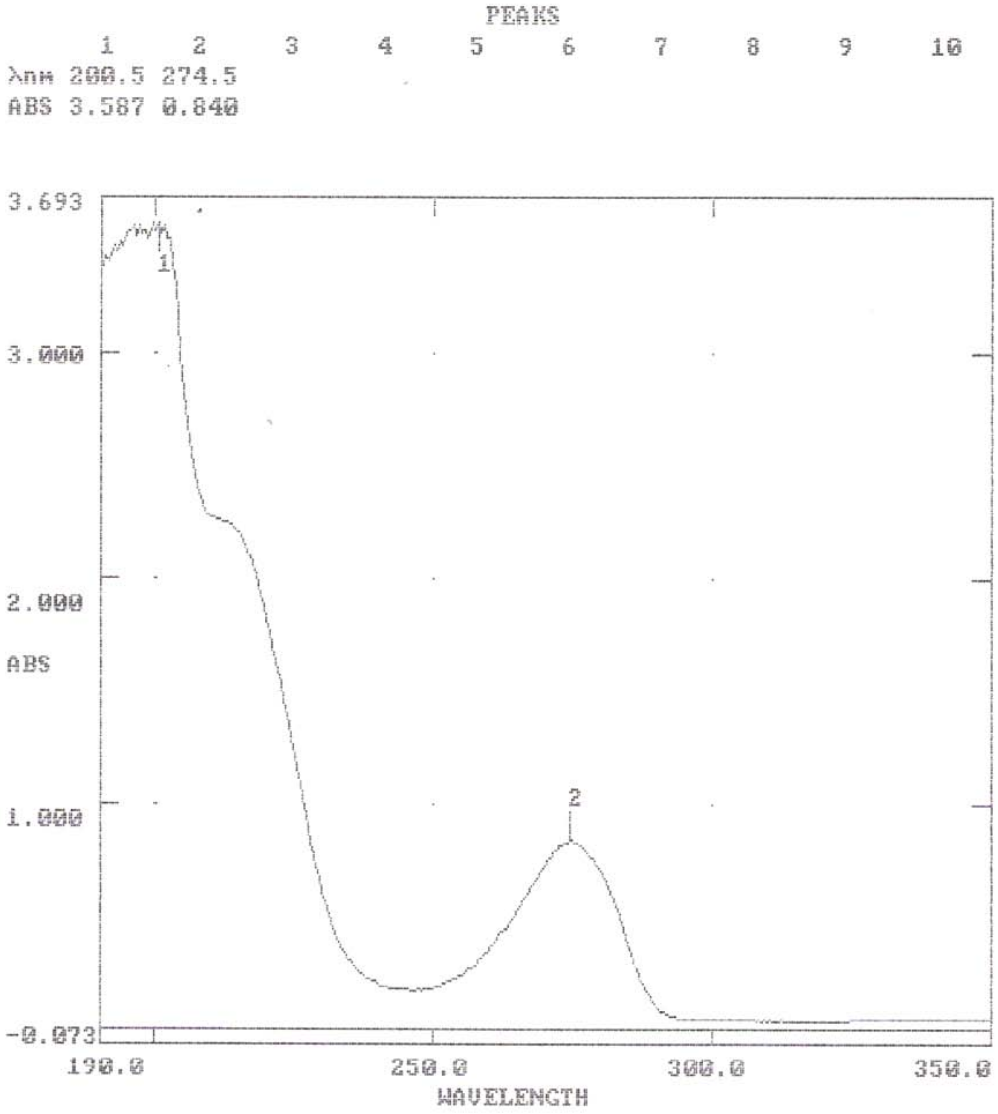


Figure 5.4 UV/Vis absorptions for Benzoquinone dissolved in water

Table 5.4 displays the data collected for the detection of catechol and benzoquinone. Figure 5.5 and Figure 5.6 display the HPLC chromatograms obtained for catechol and benzoquinone respectively.

Table 5.4 Method development data for the detection of catechol and benzoquinone

Run Number	Catechol		Benzoquinone	
	Retention Time (mins)	Peak Area	Retention Time (mins)	Peak Area
1	2.01	2820611	1.93	3913976
2	2.03	2818478	1.90	4137579
3	2.01	2803554	1.91	4056258
4	2.02	2825469	1.92	3998567
5	2.01	2820046	1.90	4002662
Average	2.016	2817631.6	1.912	4021808.4
% Error	0.89	0.53	1.22	2.45

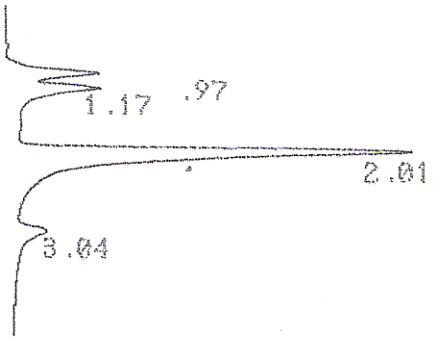


Figure 5.5 Chromatograph obtained for catechol at λ_{max} = 237.0nm

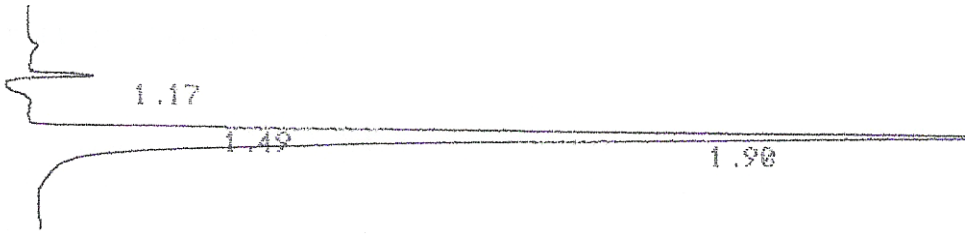


Figure 5.6 Chromatograph obtained for benzoquinone at λ_{max} = 200.5nm

The results from Table 5.4 clearly indicate that at λ_{max} = 237.0nm catechol can be detected effectively and reproducibly using HPLC. Errors in both Retention Time and Peak Area were very low at below 1%. Benzoquinone data also demonstrated good reproducibility when detecting at λ_{max} = 200.5nm with errors below 2.5% for both Retention Time and Peak Area.

5.4.3 TOC Results

The TOC results obtained for the following five experiments are shown in Table 5.5 for water and phenol controls, and Table 5.6 for catalysis.

EXP 1. Water acidified (Control)

EXP 2. Phenol acidified (Control)

EXP 3. Phenol, hydrogen peroxide and water, acidified with bubbled air (Control)

EXP 4. Hydrogen peroxide and water, acidified with bubbled air and wool catalyst (Control)

EXP 5. Phenol, hydrogen peroxide and water, acidified with bubbled air and wool catalyst (Heterogeneous Catalysis)

Table 5.5 TOC Results for Water and Phenol Controls

Experiment Number	Sample evaluated	TOC (ppm) – after 60 minutes
1	Water acidified	0.22
2	Phenol acidified	7.826

Table 5.6 TOC Results for Catalysis Controls and Heterogeneous Catalysis

Reaction Time (mins)	C_t/C_0					
	Experiment 3		Experiment 4		Experiment 5	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
0	1.000	1.000	1.000	1.000	1.000	1.000
15	0.979	0.969	1.025	1.025	0.939	0.940
30	0.945	0.940	1.040	1.040	0.689	0.689
45	0.867	0.862	1.069	1.069	0.387	0.380
60	0.858	0.860	1.176	1.176	0.347	0.347
% TOC Reduction	14.23	13.98	17.61	17.61	65.33	65.32

As can be seen from the results, the reproducibility between runs 1 and 2 was very high with all errors at less than 2%. The data given in Table 5.6 has been represented graphically in Figure 5.7.

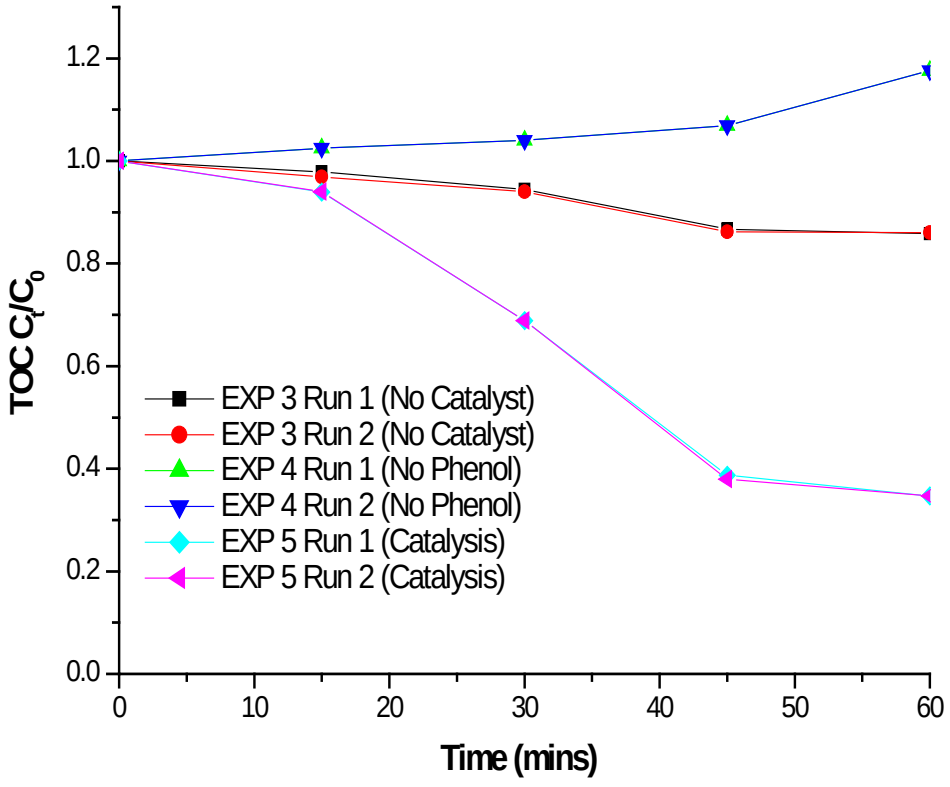


Figure 5.7 TOC Results obtained for experiments 3, 4 and 5

The TOC reduction was significantly greater with the use of the wool catalyst affording ~65% reduction compared with ~14% reduction without the catalyst. It should also be commented that there was no increase in TOC in experiment 4 (H_2O_2, bubbled air and catalyst). This suggests that during the 60 minutes the wool is not breaking down into the solution.

5.5 Conclusions

The ion chromatography results support the proposed reaction mechanism outlined in Section 1.4, Figure 1.24. As catalysis progresses the appearance and disappearance of the organic acids can be clearly observed using this technique, Figure 5.2. There were some interesting results with respect to the creation of succinic and cc-muconic acids, however the results were reproducible and it would not be impossible for these to be formed throughout the oxidation process. Unfortunately there was one unknown peak at ~9.70 minutes, which to date no identification has been found when cross-referencing with literature. Finally, data pertaining to oxalic acid may be influenced by the chlorine peak eluting at the same or similar retention time. This may also be the cause for no data being recorded for maleic acid. The chlorine peak is as a result of the impregnation and/or the hydrochloric acid used to adjust the solution to pH 3 prior to catalysis.

When using HPLC to determine Benzoquinone and Catechol, the peak resolutions obtained were good with excellent reproducibility. The errors were within acceptable limits and the retention times obtained were stable. This proposed method could now be used with confidence to determine the ring products formed in the early stages of catalysis.

Degree of mineralisation results obtained were reproducible and demonstrated that the presence of the wool catalyst produces significant reduction in TOC (~65%). This suggests that 65% of the phenol has been mineralised to carbon dioxide and water. Results indicate that during the 60 minutes of evaluation, no breakdown of wool into solution occurred as this would have been identified by an increase in TOC during experiment 4 (hydrogen peroxide and water, acidified with bubbled air and the presence of the wool catalyst).

Chapter 6 Decomposition of Industrial Effluent

6.1 Introduction

The aim of this work was to investigate the use of the wool catalyst to decompose industrial effluents containing phenolic compounds. Catalytic activity against the effluents of Chemtura and A H Marks was initially carried out in a batch reactor followed by dynamic studies where possible, to investigate catalyst performance over a prolonged period. Finally the extent to which the catalyst system could affect mineralisation by monitoring reduction in TOC was carried out for both effluents. It was hoped that the catalyst would reduce the amount of phenols in both industrial effluents as well as reduce TOC, thus reducing COD. If these objectives can be achieved this may provide an industrial application of the catalyst enabling companies such as Chemtura and A H Marks to reduce their costs further. Another benefit would be to assist in reaching the consent limits for Phenolics should the levels be lowered in the future.

6.1.1 Chemtura Corporation

Chemtura was formed in 2005 from a merger of Crompton Corporation and Great Lakes Corporation. The Chemtura site in Manchester has approximately 250 employees in research, manufacturing, sales and administration. It is a supplier of plastic additives, including flame retardants. Chemtura is a leading manufacturer in pool and spa products, and a producer of urethane polymers for all over the world. Finally, they are producers of phenol, alkylated phenols, xylenes, cresols and brominated derivatives.

The company produces 700-800 m^3 of process effluent per day with COD levels of 600ppm. They are permitted to have a COD level of up to 1500ppm. Effluent contains a mixture of phenol based chemicals. Raw process effluent enters the treatment process at pH 2. This does vary depending on the products being manufactured. The effluent is sent to a holding pit where larger particulate material is removed by sieves, this includes

plastics and other waste. Effluent lime is added to regulate the pH to between 7 and 8; this is permitted in the range pH 6-10. It is then sent to a holding tank. The effluent is then tested for phenol, COD, sediment oxygen demand (SOD), oil and grease levels prior to being sent to the settlement lagoon. Once settled waste water is sent to a local waste water treatment site. The company is billed upon the volume and COD levels of the effluent treated.

Chemtura undertook a review of their wastewater treatment system and reduced their daily discharge by half to the current levels. This was done by diverting certain waste for incineration, rather than adding to the process effluent. The total volume for treatment and the COD levels were both reduced, thus saving money. The greatest cost of the treatment process is the neutralisation (lime) and waste disposal.

The most difficult product to treat is phenol waste. Although Chemtura have an activated carbon extraction system in place to extract phenol for re-use, it still does not remove all phenols from the process effluent prior to onsite treatment. Chemtura has consent for the concentration of total phenols to be 250ppm, alkylated phenols 6-10ppm, cresols 100ppm and SOD 400ppm. Phenolics account for half the COD value (~600ppm) and this can peak to 1000-1500ppm when changes are made in the treatment system. A saving of £400 per month can be achieved by reducing COD from 1000ppm to 600ppm. Any solids are washed with petroleum ether to remove grease. No chlorinated phenolics are present in the waste; however, some brominated phenolics are present from the manufacturing of flame retardants. It is thought that the waste water effluent does not decay with time or normal storage. Data sheets provided by the company can be found in Appendix 12 to Appendix 14**.**

The analytical procedures in place use fluorescence detectors as they are very sensitive to low ppb. Calibrations are performed daily due to constant decay of the detector. UV detectors are not as sensitive, however calibration is only required once as there is no decay.

6.1.2 A H Marks and Company Limited

A H Marks is the UK's largest privately owned and independent chemical manufacturing company. It employs over 350 people and operates from a single 11 hectare site just outside Manchester. Chemicals have been produced at the site since 1877, when dyestuffs were produced for local textile industries. Today, it manufactures a wide range of specialised organic chemicals for a variety of end use sectors. Key customers include manufacturers of crop production, petrochemicals and biocides.

The annual sales turnover exceeds £65 million, and exports accounts for over 75% of the company's business interests. They have expanded sales in over 40 countries worldwide. Supporting this strong sales performance is a commitment to quality. The company is registered to ISO9001:2000 and in compliance with Good Laboratory Practice (GLP) and Investors in People (IIP) Standards. Also, they are registered to International Environmental Standard ISO14001:2004.

A H Marks produces between 3600-3700 m^3 of process effluent each week, a maximum of 35 m^3 per hour. All process effluent goes into an agitated vessel before further processing. Process effluent goes through a cone pass solvent extraction system and then neutralisation process. Raw effluent is usually around pH 1 and needs to be between pH 6 and 9 prior to disposal. The waste consists of very high concentrations of lactic acid. A H Marks extraction process uses 2-ethyl hexanol (2-EH) to remove around 80-90% of phenoxy acids and phenols. Waste is then transported off site to treatment works for disposal.

The solvent extraction process and neutralisation stage costs approximately £4 per m^3. the remaining transportation and disposal costs range £2-2.1 million per year. There has been no indication of A H Marks biologically treating the effluent. Waste that is sent for disposal must fall within the company's permit for release and is charged by volume and COD levels. Permit levels depend upon each local water authority, but there has been little change to date.

Effluent is analysed twice a day and is usually 17,600 mg/l COD. Waste tars produced from the extraction process (~1000 tonnes per year) are sent for incineration (£100-130 per tonne). The biggest drive for change in costs is that each new development or new technology is business driven. It is also necessary to work within new and existing legislation. The consent limit for phenolics is 50ppm, with phenols and chlorophenols at 20ppm and phenoxyacids at 30ppm. Consent limits will be lowering in the future. Data sheets provided by the company can be found in Appendix 15**.**

6.2 Methods

6.2.1 Static catalysis

Wool catalyst was prepared as described in previous work. The catalyst used (2g) was Crossbred, 50:50 Modified (hydrazine/hydroxylamine) with Fe/Ca standard impregnation. The iron content of the wool catalyst was 0.06mmol/g wool.

Due to the high concentration of compounds in the Chemtura effluent this was ten times diluted prior to catalysis. The volume of solution used for catalysis was 100mL containing hydrogen peroxide (122ppm). Wool catalyst and the solution were placed in a dreschel bottle with bubbled air (using compressor, 0.15 on the scale of the rotameter). Samples (20µl) were extracted at regular intervals and analysed using HPLC. A standard C-18 (250 x 4.6mm) packed column was used as the stationary phase. The mobile phase was a mixture of water (40% v/v) and methanol (60% v/v) at a flow rate of 1 mL/min. The column elute was passed through a UV detector set at 254nm.

A H Marks effluent contained a high level of lactic acid compared with the amounts of phenol present. Due to this, the effluent required a 50 times dilution for catalysis. A method was developed using HPLC to evaluate the lactic acid decomposition as this reaction could take priority over the phenol decomposition. The volume of solution used for catalysis was 100mL containing hydrogen peroxide (200ppm). Wool catalyst and the solution were placed in a dreschel bottle with bubbled air (using compressor, 0.15 on the scale of the rotameter). Samples (20µl) were extracted at regular intervals

and analysed using HPLC. For the analysis of lactic acid a standard C-18 (250 x 4.6mm) packed column was used as the stationary phase. The mobile phase was a mixture of methanol (3%) and potassium phosphate (97%) at a flow rate of 1 mL/min. The column elute was passed through a UV detector set at 220nm. Samples were also evaluated for phenol using the same HPLC parameters previously outlined.

6.2.2 Dynamic study on Chemtura effluent

Wool catalyst samples (4g) were placed in the reactor with bubbled air supplied from the bottom (45 mL min^{-1}) measured and controlled by a flow meter. A continuous flow of Chemtura effluent (20 times diluted) containing hydrogen peroxide (122ppm) was pumped through the reactor at a flow of 2 mL min^{-1}. Samples were taken from the reactor outlet at regular time intervals and analysed for phenol by HPLC. A standard C-18 (250 x 4.6mm) packed column was used for the stationary phase. The mobile phase was a mixture of methanol (40%) and double distilled water (60%) with a flow of 1 mL min^{-1}. Samples were collected from the reactor outlet and volumes of 20µl were injected and detected using UV at λ_{max}= 254nm. The sample times were 5, 15, 30, 90, 120, 180, 300 minutes and then at regular intervals until deactivation of the catalyst occurred.

6.2.3 Total Organic Carbon (TOC) evaluations

The instrumentation employed was the Analytical Science Thermalox instrument version 2.5-manual injection. The instrument was composed of a total carbon (TC) reactor carrying the Platinum coated catalyst and quartz wool loosely packed to about 10 mm, embedded in an oven. The carrier gas was oxygen. Carbon dioxide produced was analysed using a Non-Diffusive Infra-Red (NDIR) gas analyser. The instrumental parameters were as follows:

- Carrier gas flow rate: 180 mL/min
- Oven temperature: 680 ^{o}C
- Target CV %: 4

Number of repeats if CV was not achieved: 2

A calibration of TOC was performed using dilutions of potassium hydrogen phthalate (KPH) with acidified water (containing 0.1% HCl). Solutions were sparged with oxygen for 3 minutes in order to displace any dissolved CO_2. 30µL of each standard dilution was injected into the reactor and the TC and TIC recorded allowing TOC to be calculated by subtraction. Seven injections of each standard solution were required and the mean of the five best correlation measures considered. Samples collected from the static catalysis reactor outlet were prepared and analysed in the same manner.

The conditions for the experiment were as outlined in the static catalysis method. Due to the long reaction times found in static catalysis of both effluents, samples were extracted on a daily basis and analysed for TOC as previously described. A control run was completed using the fresh feed prepared and analysed in the same manner; however using H_2O_2 but with no catalyst included. This would provide the TOC data for the reaction between each effluent and hydrogen peroxide.

6.3 Results

6.3.1 Static catalysis

Calibration data was obtained for phenol in the same manner as previously discussed in Section 3.3.1. This evaluation concluded that the concentration of phenol can be calculated using the following equation: **y** = 2229.9**x** - 3829.6, where y = peak area; x = concentration of phenolic compound, ppm. Results for the Chemtura effluent are presented in Table 6.1 and Figure 6.1.

Table 6.1 Phenolic compound oxidation of Chemtura effluent using Fe-wool catalyst

Effluent Sample	Duration of treatment	HPLC data for Phenolic Compound	
		Retention time, Min	Peak Area
Catalysis (Fe-Wool, H_2O_2)			
1	0 min	2.626 2.582	15391.55 16351.42
2	10 min	2.660 2.645	14600.34 14627.95
3	30 min	2.701 2.687	15603.36 15266.09
4	1 hr	2.804	14409.08
5	2 hr	2.683	3646.94
6	4 hr	2.734	109.25
7	6 hr	2.695	Not detectable
8	21 hr	2.68	96.40
9	24 hr	2.68	68.65
No catalyst, but H_2O_2 presence			
1C	0 min	2.858 2.858	16404.72 16284.99
2C	10 min	2.86 2.848	15772.40 16029.99
3C	30 min	2.842 2.838	16121.51 16442.47
4C	1 hr	2.884 2.821	15333.19 16066.64
	1.5 hr	2.826 2.914	15713.42 14920.59
	2 hr	2.870 2.823	14967.47 14648.10
9C	24 hr	2.540 2.577	13039.42 13365.54

Fe-wool catalyst (2g) was Crossbred 50:50 Modified (hydrazine/hydroxylamine) with Fe^{3+}/Ca^{2+} impregnation [Fe] = 0.06mmol/g wool, effluent (100mL), [H_2O_2] = 122ppm

Figure 6.1 indicated that the phenolic components of Chemtura effluent can be no longer be detected by HPLC after 24 hours after catalysis. This is a promising result in identifying an industrial application for the wool catalyst.

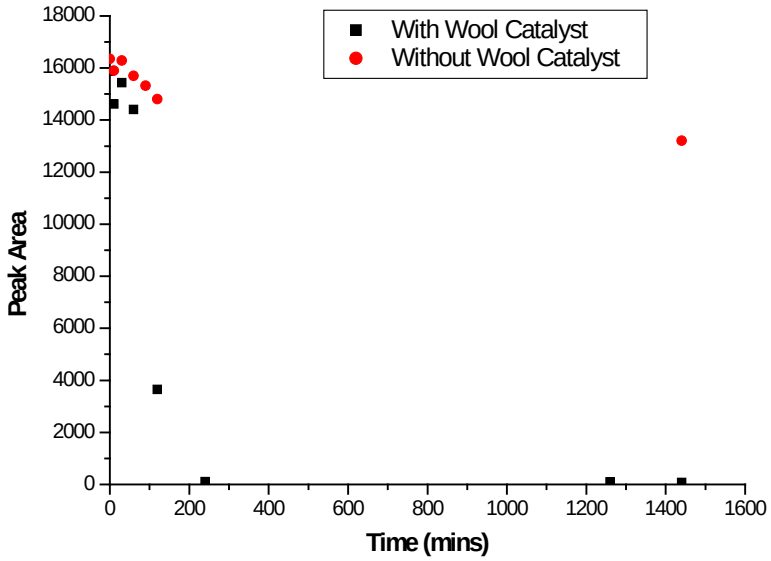


Figure 6.1 Graphical representation of phenolic compound oxidation of Chemtura effluent using Fe-wool catalyst. Fe-wool catalyst (2g) was Crossbred 50:50 Modified (hydrazine/hydroxylamine) with Fe^{3+}/Ca^{2+} impregnation [Fe] = 0.06mmol/g wool, effluent (100mL), [H_2O_2] = 122ppm

Results for the catalysis of A H Marks effluent are presented in Table 6.2 and Figure 6.2. Background research and information provided by A H Marks clearly demonstrated that high concentrations of lactic acid could be found in the effluent prior to catalysis. This information lead to the results in Figure 6.2 which demonstrate the reduction in lactic acid and phenolic compounds during catalysis.

Table 6.2 Lactic acid and Phenol oxidation of A H Marks effluent using Fe-wool catalyst

Time (mins)	C_t/C_0			
	Control (Lactic Acid)	Lactic Acid	Control (Phenol)	Phenol
0	1.00	1.00	1.00	1.00
30	1.00	0.85	0.99	1.00
60	1.00	0.83	0.98	0.98
120	1.00	0.80	0.90	0.96
180	0.98	0.78	0.87	0.96
240	0.98	0.78	0.85	0.95
300	0.98	0.76	0.84	0.93
360	0.96	0.73	0.83	0.91
420	0.95	0.72	0.83	0.86
480	0.95	0.72	0.82	0.85
1440	0.93	0.72	0.82	0.81
1800	0.93	0.71	0.82	0.80
2880	0.91	0.70	0.81	0.80
3240	0.90	0.69	0.81	0.79
4320	0.88	0.69	0.80	0.69
4680	0.87	0.68	0.80	0.68
5760	0.85	0.64	0.79	0.65
6120	0.85	0.62	0.78	0.53
7200	0.85	0.54	0.78	0.49

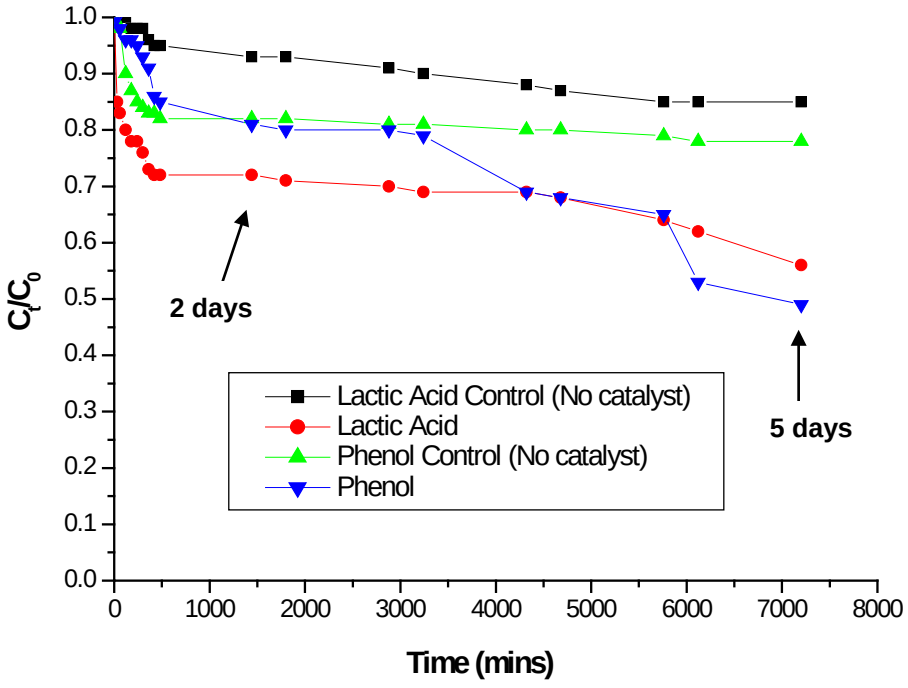


Figure 6.2 The oxidation of A H Marks effluent using Fe-wool catalyst where C_t = concentration at time t and C_0 at time 0mins.

Unlike the Chemtura effluent the concentration of compounds in the A H Marks effluent was much greater. With this in mind it came as no surprise that after 5 days the reduction in lactic acid and phenolics was 46% and 51% respectively. This result is again very positive. It identifies an industrial application which could be optimised further. Due to the long retention time during catalysis, dynamic analysis would not be possible with the reactors currently available at the University.

6.3.2 Dynamic Study on Chemtura Effluent

The data collected for the dynamic investigation of Chemtura effluent is given in Table 6.3 and represented graphically in Figure 6.3.

Table 6.3 Dynamic data for the catalysis of Phenol in Chemtura effluent using Fe-wool catalysts

Time (mins)	C_t/C_0
0	1.00
5	0.94
15	0.67
30	0.44
90	0.45
120	0.39
180	0.00
300	0.00
420	0.03
480	0.00
540	0.00
600	0.00
660	0.00
720	0.00
780	0.00
840	0.00
900	0.00
1020	0.00
1200	0.00
1380	0.00
1560	0.00
1680	0.76
1800	0.76
1860	0.74
1920	0.91
1980	0.95

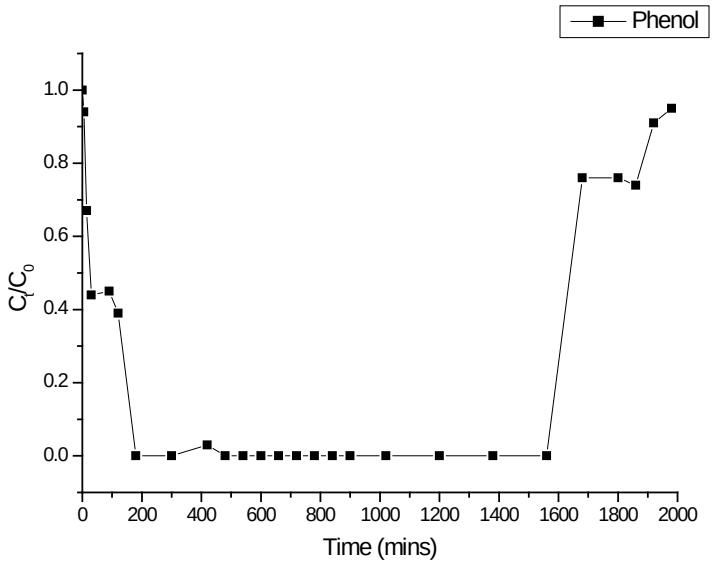


Figure 6.3 Decomposition of phenol in Chemtura effluent using a flow reactor, Flow = 2 ml/min, [Fe content] = Variable, [H_2O_2] = 122ppm and wool = 4g

Figure 6.3 demonstrates that the catalyst performed reasonably well against the industrial effluent provided by Chemtura. For approximately 1400minutes (23.3 hours) phenol could not be detected in solution by HPLC. Considering the high concentration of this effluent compared to previous dynamic studies in a phenol system, the lifetime was promising at 33 hours. With optimised hydrogen peroxide concentrations this could potentially be improved further.

In order to draw meaningful conclusions from the data collected the following calculations were required,

- The yield degree of the substance (α),
- Mass of the substance decomposed (M)
- Turn-over frequency (TOF)

These were determined in the same manner as previously described in Section 3.5.2. This data is summarised in Table 6.4.

Table 6.4 Parameters for the oxidation of phenol from the dynamic data for Chemtura effluent

Parameter	Value
Area	1617.98
The yield of degree of the substance	0.860
Amount Phenol Decomposed (mmol)	0.324
[Fe] content (mmol/g wool)	0.06
Amount Catalyst (4g)	4.00
Catalyst Lifetime (min)	1980
Turn-over Frequency (min^{-1})	$0.682x10^{-3}$

This data converted to a TOF of 0.682×10^{-3} min^{-1} compared to $2.9x10^{-3}$ min^{-1} achieved using the corresponding catalyst when evaluating phenol previously (Section 3.4.2).

6.3.3 Total Organic Carbon (TOC) Evaluations

The TOC reduction in both effluents and their respective controls was evaluated over 5 days. Reduction of TOC is clearly demonstrated in Table 6.5 and Figure 6.4.

Table 6.5 TOC reduction for static mode catalysis of Chemutra and A H Marks Effluents with time

Reaction Time (Days)	C_t/C_0			
	Chemtura Control	Chemtura Catalysis	A H Marks Control	A H Marks Catalysis
0	1.00	1.00	1.00	1.00
1	0.98	0.82	1.00	0.97
2	0.96	0.56	0.99	0.83
3	0.93	0.24	0.99	0.81
4	0.91	0.24	0.98	0.72
5	0.89	0.24	0.98	0.67
% TOC Reduction	**11**	**76**	**2**	**33**

Fe-wool catalyst (2g) was Crossbred 50:50 Modified (hydrazine/hydroxylamine) with Fe^{3+}/Ca^{2+} impregnation [Fe] = 0.06mmol/g wool, effluent (100mL), Chemtura [H_2O_2] = 200ppm, A H Marks [H_2O_2] = 200ppm

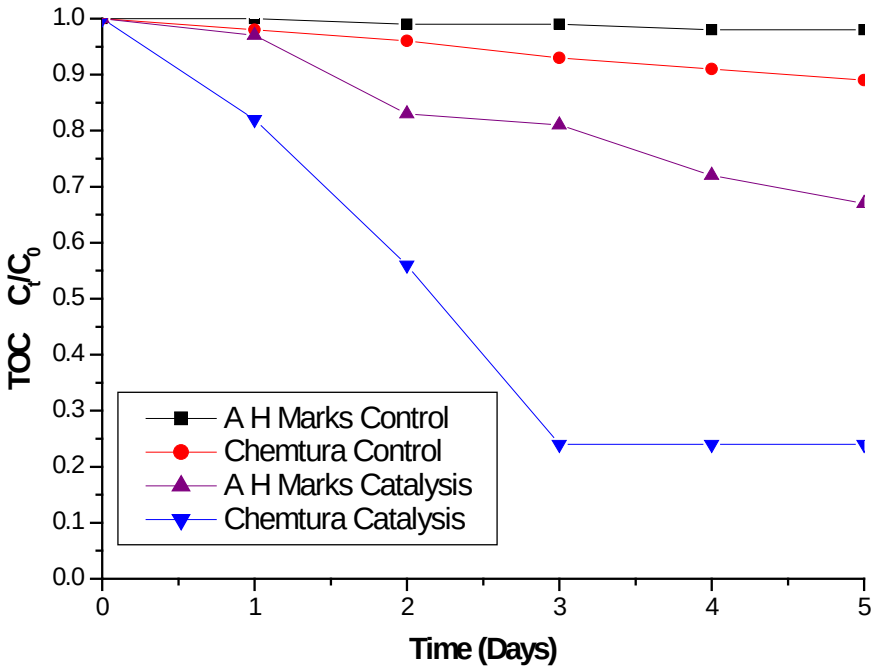


Figure 6.4 Graphical representation of the TOC results for both Chemtura and A H Marks Effluent Fe-wool catalyst (2g) was Crossbred 50:50 Modified (hydrazine/hydroxylamine) with Fe^{3+}/Ca^{2+} impregnation [Fe] = 0.06mmol/g wool, effluent (100mL), Chemtura [H_2O_2] = 200ppm, A H Marks [H_2O_2] = 200ppm

It can be clearly observed that the presence of the wool catalyst reduces the TOC for both Chemtura and A H Marks effluents. After three days the TOC is reduced by 76% for the Chemtura effluent. The reduction in TOC for A H Marks is lower and slower at 33% after 5 days. However, the substances present in the effluent were very varied and in some cases, very high concentrations (Appendix 15). It may be that when employing a greater amount of catalyst the TOC could be reduced further at a faster pace.

6.4 Conclusions

The catalyst performed best against the Chemtura effluent in all areas, with phenol reduction of 100% in 4 hours in the static catalysis evaluation and the reaction time was short enough to enable a dynamic investigation to be performed. TOC was also

significantly reduced (76%) in Chemtura effluent after 3 days compared with 33% reduction in A H Marks effluent (5 days). This may be improved further by re-dosing hydrogen peroxide throughout catalysis.

Static analysis of catalyst performance against A H Marks waste water showed that after five days approximately 50% of both the lactic acid and phenol content were reduced. It must be mentioned that in both cases the effluent had been significantly diluted (50 times dilution). Due to the extended reaction time dynamic investigations for A H Marks were not possible in the available dynamic rig.

Catalyst longevity evaluations against the Chemtura effluent identified a lifetime of 33 hours. Although the lifetime of the catalyst was reduced compared with a phenol system, 49 Hours, results are positive and do identify an industrial application. Reduction in lifetime is likely to be attributed to the concentration and presence of other substances in the effluent. This was further supported by achieving a TOF of 0.682 x 10^{-3} min^{-1} compared to ~2.9x10^{-3} min^{-1} achieved in the phenol system (Section 3.4.2). Catalysis longevity may be affected by the other chemicals in the effluent (see Appendix 15). These may cause competition during catalysis and potentially possibly block sites leading to deactivation.

Chapter 7 General Conclusions and Future Work

7.1 Summary of Findings

The following comments are the main findings with regards to the development of a solid phase catalyst supported on wool for the treatment of industrial wastewater. These include references to scouring methods, Fe (III) uptake, chemical modification, catalytic activity, physical/chemical characterisation work, confirmation of products of catalysis and performance against real industrial effluents.

It has been concluded that non-ionic detergent scouring methods have greater success in the removal of dirt and grease compared with solvent/water degreasing methods. When performing laboratory scouring, no alkali addition was required. Higher Fe (III) uptakes were achieved when using non-ionic scouring samples than from solvent degreasing.

Modification of wool fibre at pH 9.5 caused significant destruction of fibres. Samples became fragile post modification, especially Woolmark fibres. A less friable fibre was achieved when modifying at pH 7. Chemical modification at pH 7 allowed for greater Fe (III) uptake, with the greatest being achieved when using hydroxylamine modified wools. Similar amounts of Fe (III) uptakes were observed for each of the three modification regimes independent of wool type. When modification was carried out at pH 7, it was found that little or no iron was removed from the wool when exposed to Na_2-EDTA for 24 hours regardless of wool type.

Woolmark, DEFRA and Crossbred wool samples when modified with hydroxylamine are able to decompose phenol by 98-100% after 60 minutes. In all three cases, very low levels of homogeneous catalysis were present at 20%, 8% and 3% respectively. This was replicated in all cases over three cycles.

Wool samples which had not been modified yielded very high levels of homogeneous catalysis or a generally low level of catalytic activity. It was found that coloured wools

(i.e. grey/black haired sheep) had poor Fe (III) fixation, leading to high homogeneous levels of catalysis following the leaching of iron into solution. In the case of the Dark Grey Herdwick samples modified with hydroxylamine poor results were obtained. It was identified that phenol decomposition arose from homogeneous catalysis. The 50:50 (hydroxylamine and hydrazine) modified sample performed better, but the homogeneous contribution was somewhat higher than the corresponding Woolmark and DEFRA samples at between 25-35% for mill scoured samples and 50-100% for the laboratory scoured samples. It is not clear at this stage why the Herdwick behaved this way. The proportion of grease on its outer surface is greater than others prior to scouring, it has a high percentage of melanin, it is coarser and breaks on handling to a greater extent than other wools.

Investigations using hydroxylamine modified and Fe (III) impregnated Crossbred wool indicated that between 98% and 100% phenol disappearance could be achieved using either laboratory or mill scoured samples. The homogeneous contribution was found to be less than 10% and at best only 2%. It was also observed that the wool acted poorly as a catalyst for the first two cycles of static batch evaluations. This possibly indicates a conditioning of the catalyst during the first two hours or is simply a wettability issue. Halfbreds and Blackface samples were treated in the same manner resulting in the same observations. The maximum phenol decompositions achieved using these samples were 90% and 80% respectively. Homogeneous contribution to catalysis was less than 22% for Halfbreds and 35% for Blackface. Excellent batch-to-batch reproducibility was found in all three wools.

Although the exact costs of the Woolmark and DEFRA wools are unknown it is known that they are more expensive than the Crossbred wool. Woolmark has undergone previous processing such as bleaching which increases the cost per kilogram. The DEFRA wool is a ‘top-wool’ and is a higher quality than the others investigated. Crossbred wool costs £1.60 per kilogram of scoured wool and was the preferred sample.

Optimum static batch conditions were found to be achieved when using 1.0g of wool catalyst. 100% phenol disappearance after 50 minutes was achieved and sustained over

three cycles. Homogeneous contribution to catalysis was low at between 2% and 6%. The increased H_2O_2 concentration (from 50ppm to 122ppm) did not appear to affect the catalyst performance.

Using the improved impregnation techniques did not result in additional Fe (III) loading, nor did it noticeably affect leaching. During dynamic evaluation of samples, no iron was detected in solution phase throughout catalysis, suggesting little or no homogeneous contribution to catalysis. This was further confirmed when analysing deactivated wool catalysts for iron content. On comparing these results, the change in iron content was minimal at ±3.0%. Impregnation with Fe (III) / Ca or Fe (III) / Li increased the catalyst lifetime from ~40 hours to 49 hours and 60 hours respectively. An increase in the Turn-Over Frequency (TOF) was also observed from ~2.7 x 10^{-3} min^{-1} to ~2.9 x 10^{-3} min^{-1} (TOF values for Fe (III) / Ca and Fe (III) / Li were similar). Results obtained for Dark Grey Herdwick were still poor when investigating dynamically. The TOF was low at 1.197 x 10^{-3} min^{-1} and it can be concluded that this wool was not suitable for further analysis.

Fibre diameter results yielded no correlation between diameter and catalytic performance (static batch mode). DEFRA, Woolmark and Crossbred samples perform well as a a catalyst when modified with hydroxylamine and impregnated with Fe (III). However, they all have different fibre diameters. DEFRA was the thickest at 40.3 µm, Crossbred 34.1 µm and Woolmark the finest at 23.5 µm. No clear trend was observed in the other data obtained using the Laserscan.

As expected, the most significant loss in tensile strength was observed after modification. Treatment involved in modifying the fibres was the most intensive even when adjusting to pH 7. Fortunately, there was no major loss in strength after modification or deactivation.

SEM/EDX results indicated that fibres modified with hydroxylamine or a 50:50 hydrazine/hydroxylamine mixture had minor changes to the surface of the cuticle scale. A ‘peeling affect’ can be observed on the outermost layer of the cuticle. This was more

pronounced with hydroxylamine modified samples where peeled scales from branches between fibres in the sample. EDX confirmed the presence of Fe and Cl from the impregnating solution, ferric chloride. Cross-sectional and longitudinal sections of the fibres confirmed that both Fe and Cl were present at the external layers and also the interior of the wool fibre. Unfortunately no significant changes in wool were observed using IR-ATR as a result of treatment in the frequency range 500 cm^{-1} – 4000 cm^{-1}. On considering the cross-sectional results obtained from the SEM/EDX work, iron can be clearly detected throughout the fibre. Thus, impregnation is not limited to the surface which may also indicate that is also the case for modification. IR-ATR is a surface analysis technique and therefore it is possible that the surface concentration of that which is of interest may be too low for this technique.

Ion chromatography results support the proposed mechanism from literature outlined in Section 1.4 (Figure 1.24). As catalysis progresses the appearance and disappearance of organic acids can be clearly observed with this technique. Data pertaining to oxalic acid may be influenced by the chlorine peak eluting at the same or similar retention time. This would also afford an explanation as to why no results were obtained for maleic acid. The chlorine peak arises as a result of impregnation and/or the hydrochloric acid used to pH adjust prior to catalysis

TOC results obtained were reproducible and demonstrated that the presence of the wool catalyst reduces TOC significantly by ~65%. This suggests that approximately 65% of the phenol has been mineralised to carbon dioxide and water. Results also indicated that during the 60 minutes of evaluation, no breakdown of wool into solution occurred as this would have been identified by an increase in TOC during experiment 4 (hydrogen peroxide, 122 ppm, acidified water with bubbled air and the presence of the wool catalyst).

Finally the catalyst performed well against Chemtura effluent in all areas. Phenol could no longer be detected after 24 hours in the static catalysis evaluation and the reaction time was of a sensible length. This allowed for a dynamic investigation to be carried out. TOC could be significantly reduced (76%) in Chemtura effluent after 3 days

compared with 33% reduction in A H Marks effluent after 5 days. Static analysis of catalyst performance against A H Marks waste water showed that after five days approximately 50% of both lactic acid and phenol content were reduced. Due to the extended reaction time dynamic investigations were not possible for A H Marks effluent in the available dynamic rig.

7.2 Further Work

Unfortunately results were very limited when attempting to chemically characterise the wool samples. It was hoped that IR-ATR would be able to illustrate the chemical changes that took place at the various stages of processing. It has been theorised that such changes in the fibre were not limited to the surface of the fibre and therefore the concentration changes on the surface may be two subtle for IR-ATR to be effective. IR-ATR is a surface specific analytical technique. It may be that traditional IR and Raman Spectroscopy could provide more detailed information should the sample preparation be appropriate and lend itself to this form of analysis. Other techniques that may provide chemical information for wool samples include UV Reflectance and NMR.

To date very little information has been found in literature with regards to catalyst regeneration. In the papers found, the regeneration process has involved high temperatures (BUTT and PETERSON, 1988; Hwang et al., 2001; Jeong et al., 2004; Ohishi et al., 2005). It is assumed that the spent catalyst has a bi-product of catalysis blocking the active site. In a lot of cases, regeneration via either oxidation or reduction may require elevated temperatures. This can prevent the active site returning to its original state (BUTT and PETERSON, 1988). In the case of wool it is not desirable to use high temperatures as this could lead to complete destruction of the fiber supporting the active sites. Hwang et al. (2001) investigated the regeneration of Fe-K/alumina catalyst using three treatments; solvent extraction (methylene chloride), reduction and oxidation-reduction. They found the solvent extraction treatment to be poor. When treating the spent catalyst with oxidation-reduction at 450^{o}C it continued to perform as a fresh catalyst. Research has also been carried out for the regeneration (with heat) of Cr-MCM-41 catalyst used in the dehydrogenation of ethylbenzene (Ohishi et al., 2005).

After deactivation a mixture of O_2/N_2 was applied to the catalyst for one hour. The activity towards ethylbenzene was recovered after treatment for multiple regenerations. Jeong et al. (Jeong et al., 2004) investigated the regeneration of a TiO_2 catalyst using ultra-violet irradiation. The catalyst was deactivated by photo-degradation of toluene under 365nm irradiation (2 hours). Regeneration was performed by irradiation with 254 and 185nm UV in humid air or nitrogen for 30 minutes (residence time was 33s). It was found that when using humid air the conversion ratio of toluene was restored completely and the TiO_2 surface restored to its original colour.

Previous work has been carried out at De Montfort University to investigate the regeneration of a novel PAN catalyst. The use of acetic acid and hydrochloric acid was evaluated. It was found that HCl performed better as a regenerate; however the study was brief and required optimisation. The following chemicals could be used as regenerates for the wool catalyst:

- Phosphoric acid
- Hydrochloric acid
- Hydrogen Peroxide

The work would be carried out with predominantly acids due to the reaction of wool at alkaline pH. Treatment with these chemicals could help re-oxidise the iron and open up blocked sites ready for catalysis. Parameters such as concentration, pH and length of exposure could be varied to determine optimum conditions. However, it is desirable to keep the pH in the range pH 3-9. Outside this could give rise to extensive fibre damage. An initial indication of suitable conditions could be determined by evaluation of regenerate solutions after exposure to investigate iron leaching from the catalyst into solution. This could then be followed by the evaluation of static catalytic performance against phenol over three cycles. Samples which have poor activity would then be excluded from further study. Once a set or couple of sets of optimised conditions are established dynamic studies would then be required to evaluate the longevity of the regenerated catalyst.

Another study which may be of interest would be to investigate the hydrogen peroxide expenditure (or usage) throughout catalysis. This can be carried out using the static batch analysis methods already established. It is possible to analyse for hydrogen peroxide using HPLC. The method employed for the quantification of phenol would in fact be suitable with an adjustment to the UV detection. A study in this area would also lend itself to investigate the affect of hydrogen peroxide dosing throughout catalysis. With further hydrogen peroxide usage data, extensive kinetics information can then also be gained for the catalysis.

Further investigations of the products formed during catalysis would provide a more complete picture. In addition to the Ion Chromatography study performed, it would be of great interest to conduct evaluations using Liquid Chromatography Mass Spectroscopy (LC-MS). This would allow for a more informed analysis of products and identify any unknowns. It also overcomes the problems encountered with the presence of Chlorine as a result of impregnation. Benzoquinone and catechol also require investigation by High Performance Liquid Chromatography (HPLC). This could be done in the same manner as the Ion Chromatography work adopting the HPLC conditions and methodology reported in Section 5.4.2.

Finally, Chemical oxygen demand (COD) is one of the most widely used analysis / parameters in the characterisation of wastewater. It gives an indication of the degree of organic loading in the sample under investigation. It is a measure of the quantity of oxygen required for the oxidation of reduced species, including organic matter in water samples, using a specific oxidizing agent, temperature and reaction length. Most types of organics are oxidised by a boiling mixture of chromic and sulphuric acid, Hach Method (HACH, 2008) resulting in the solution changing colour which can be quantified by UV/VIS.

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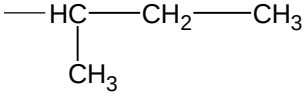
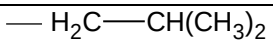
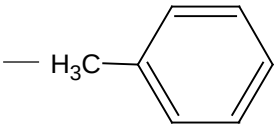
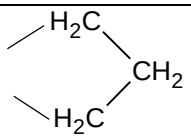
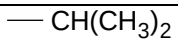
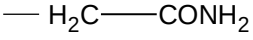
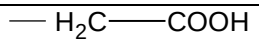
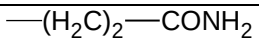
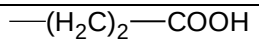
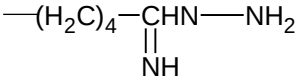
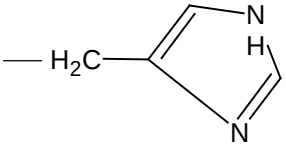
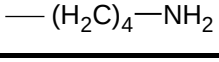
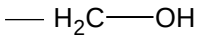
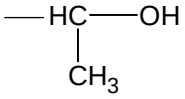
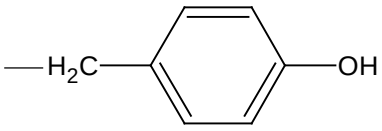
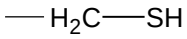
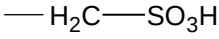
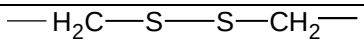
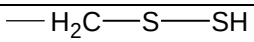
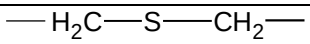
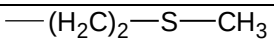
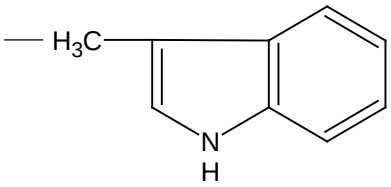
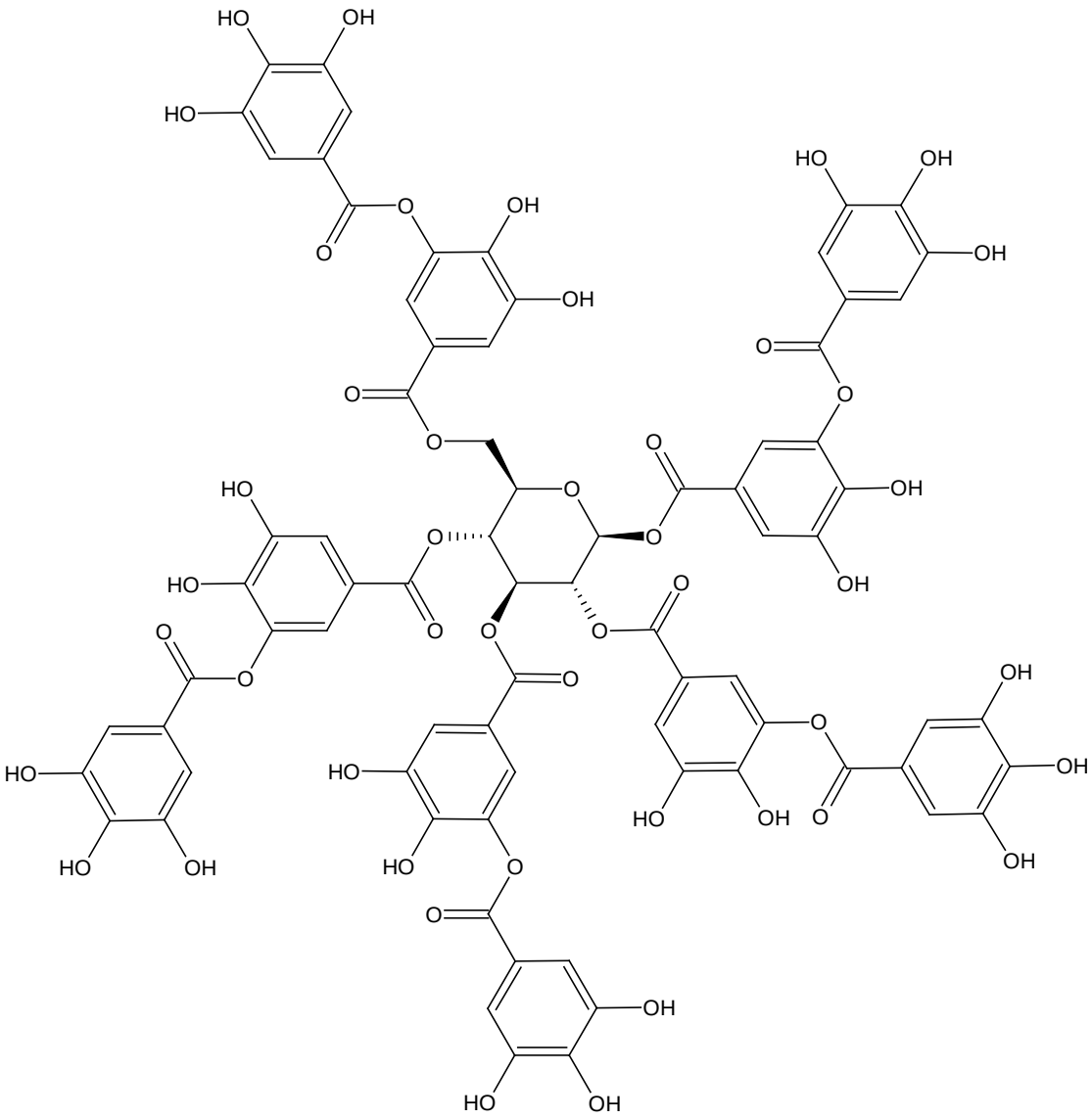
Appendices

Appendix 1 - Amino acid side chains (R)

Amino Acid (AA)	Side Chain
INERT Alanine	
Glycine	
Isoleucine	
Leucine	
Phenylalanine	
Proline	
Valine	
ACIDIC (and their ω-amides) Asparagine	
Aspartic Acid	
Glutamine	
Glutamic Acid	
BASIC Arginine	
Histidine	
Lysine	

HYDROXYL Serine	
Threonine	
Tyrosine	
SULPHUR-CONTAINING Cysteine	
Cysteic acid	
Cystine	
Thiocysteine	
Lanthionine	
Methionine	
MISCELLANEOUS Tryptophan	

Appendix 2 - Chemical Structure of Tannic Acid ($C_{76}H5_2O_{46}$)

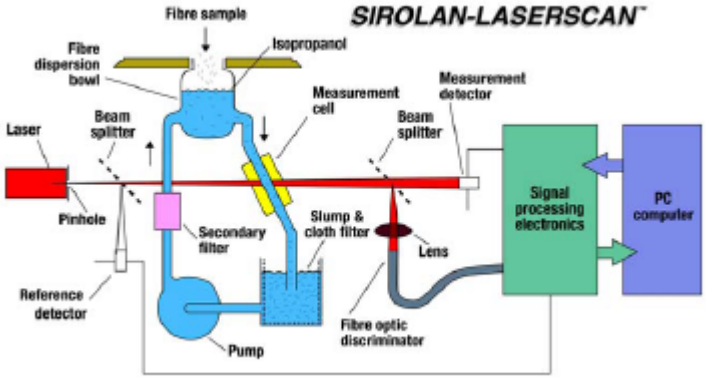


Appendix 3 - Dynamic Studies Data for Crossbred, DEFRA and Dark Grey Herdwick Wool Catalysts

Time (mins)	C_t/C_0						
	Crossbred (Fe^{3+}) Batch 1	Crossbred (Fe^{3+}) Batch 2	DEFRA (Fe^{3+})	Crossbred (Fe^{3+}/Ca)	Crossbred (Fe^{3+}/Li) Batch 1	Crossbred (Fe^{3+}/Li) Batch 2	DGH (Fe^{3+})
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00
5	0.35	0.35	0.34	0.42	0.38	0.36	0.99
15	0.28	0.23	0.28	0.30	0.29	0.27	0.92
30	0.03	0.04	0.03	0.12	0.23	0.20	0.81
90	0.00	0.10	0.00	0.07	0.20	0.18	0.74
120	0.11	0.09	0.11	0.06	0.14	0.14	0.63
150	0.09	0.09	0.09	0.02	0.10	0.10	0.66
180	0.06	0.10	0.07	0.01	0.06	0.07	0.61
210	0.11	0.11	0.13	0.03	0.06	0.06	0.63
240	0.02	0.03	0.02	0.05	0.05	0.06	0.58
300	0.03	0.03	0.03	0.02	0.05	0.05	0.56
360	0.07	0.08	0.07	0.01	0.04	0.04	0.50
390	0.08	0.11	0.08	0.01	0.04	0.04	0.52
420	0.11	0.11	0.11	0.01	0.03	0.03	0.53
480	0.07	0.07	0.07	0.04	0.03	0.03	0.53
510	0.06	0.05	0.07	0.04	0.03	0.03	0.58
540	0.05	0.04	0.05	0.03	0.04	0.04	0.60
600	0.05	0.05	0.05	0.03	0.04	0.04	0.66
660	0.01	0.02	0.01	0.02	0.04	0.03	0.71
720	0.01	0.02	0.01	0.03	0.03	0.03	0.78
750	0.01	0.01	0.01	0.02	0.03	0.03	0.79
780	0.04	0.03	0.03	0.00	0.02	0.02	0.80
840	0.06	0.04	0.06	0.03	0.02	0.01	0.81
900	0.06	0.06	0.06	0.05	0.01	0.01	0.81
960	0.00	0.03	0.00	0.04	0.01	0.01	0.82
1020	0.01	0.00	0.01	0.01	0.01	0.01	0.83
1050	0.00	0.00	0.01	0.05	0.01	0.01	0.85
1080	0.07	0.05	0.08	0.08	0.01	0.01	0.85
1140	0.30	0.06	0.28	0.08	0.01	0.01	0.86
1200	0.36	0.22	0.38	0.08	0.01	0.01	0.89
1260	0.35	0.25	0.38	0.02	0.03	0.01	0.91
1290	0.36	0.32	0.38	0.08	0.05	0.02	0.93
1320	0.30	0.39	0.41	0.13	0.07	0.02	0.96
1380	0.30	0.38	0.36	0.12	0.09	0.04	0.97
1470	0.28	0.28	0.34	0.09	0.09	0.06	0.97
1530	0.24	0.21	0.25	0.10	0.07	0.08	
1560	0.22	0.22	0.22	0.06	0.07	0.08	

Time (mins)	C_t/C_0						
	Crossbred (Fe^{3+}) Batch 1	Crossbred (Fe^{3+}) Batch 2	DEFRA (Fe^{3+})	Crossbred (Fe^{3+}/Ca)	Crossbred (Fe^{3+}/Li) Batch 1	Crossbred (Fe^{3+}/Li) Batch 2	DGH (Fe^{3+})
1590	0.23	0.24	0.33	0.06	0.06	0.06	
1650	0.21	0.22	0.3	0.07	0.06	0.06	
1710	0.19	0.17	0.21	0.07	0.06	0.06	
1770	0.22	0.23	0.26	0.08	0.06	0.06	
1800	0.25	0.26	0.31	0.09	0.07	0.06	
1860	0.06	0.07	0.07	0.11	0.07	0.06	
1920	0.07	0.07	0.09	0.12	0.07	0.07	
1980	0.08	0.07	0.08	0.13	0.08	0.07	
2040	0.14	0.12	0.17	0.14	0.08	0.08	
2070	0.20	0.13	0.24	0.15	0.09	0.09	
2100	0.37	0.20	0.43	0.16	0.09	0.09	
2160	0.40	0.34	0.46	0.18	0.09	0.09	
2220	0.55	0.55	0.59	0.19	0.10	0.09	
2280	0.76	0.66	0.80	0.20	0.10	0.09	
2340	0.84	0.77	0.86	0.22	0.11	0.10	
2400	0.86	0.87	0.91	0.24	0.11	0.10	
2430	0.97	0.95	0.95	0.26	0.11	0.11	
2460	0.97	0.96	0.96	0.29	0.11	0.11	
2520	0.97	0.96	0.96	0.32	0.12	0.11	
2580				0.34	0.12	0.12	
2640				0.37	0.12	0.12	
2700				0.40	0.12	0.12	
2760				0.48	0.14	0.15	
2820				0.61	0.16	0.15	
2880				0.75	0.18	0.15	
2940				0.97	0.22	0.21	
3000					0.26	0.26	
3060					0.33	0.29	
3120					0.41	0.39	
3180					0.50	0.45	
3240					0.58	0.53	
3300					0.65	0.60	
3360					0.70	0.64	
3420					0.83	0.72	
3480					0.90	0.73	
3540					0.95	0.95	
3600					0.98	0.98	

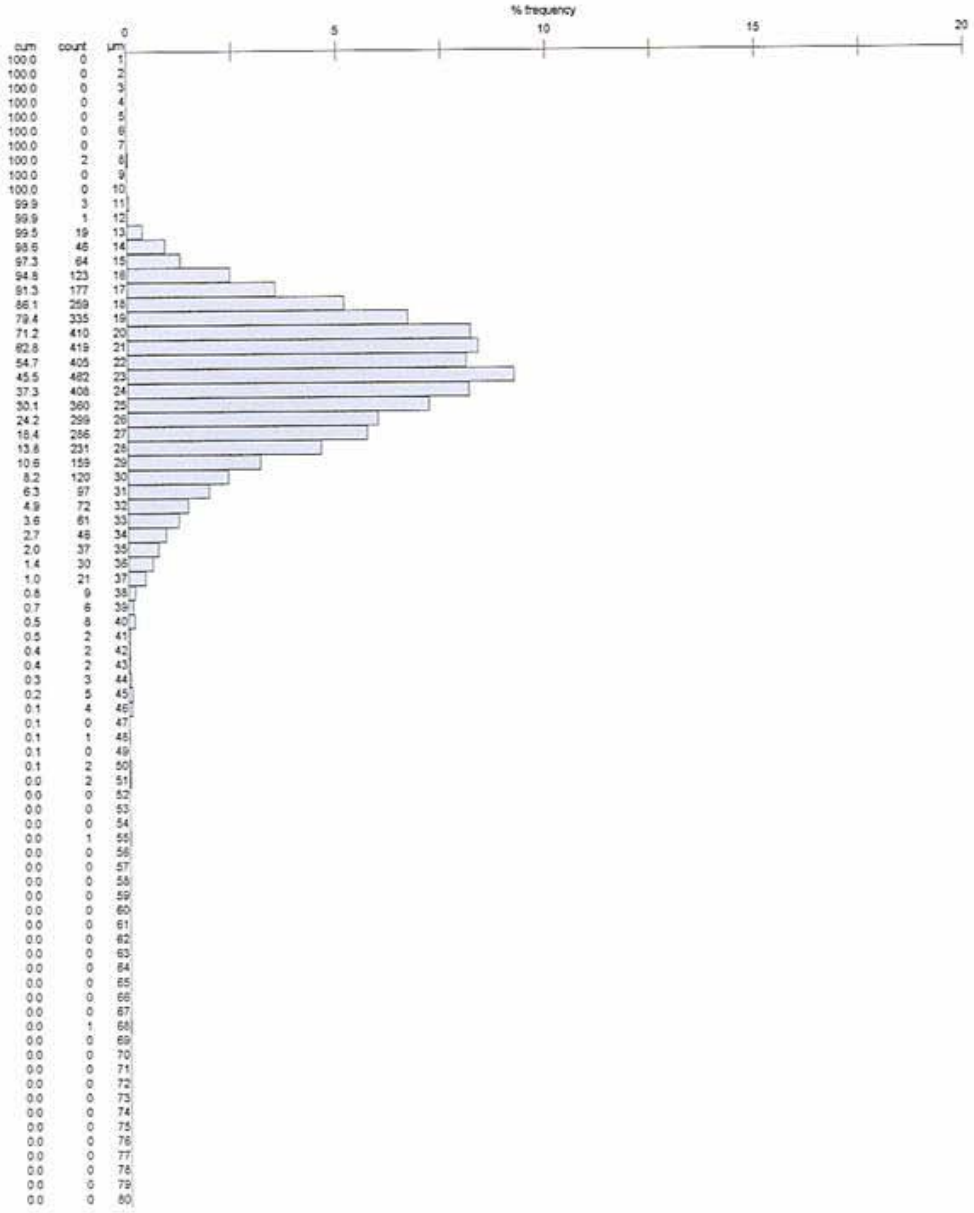
Appendix 4 - Schematic diagram of the Laserscan



Appendix 5 - WOOLMARK Fibre Diameter Results

AWTA Laserscan

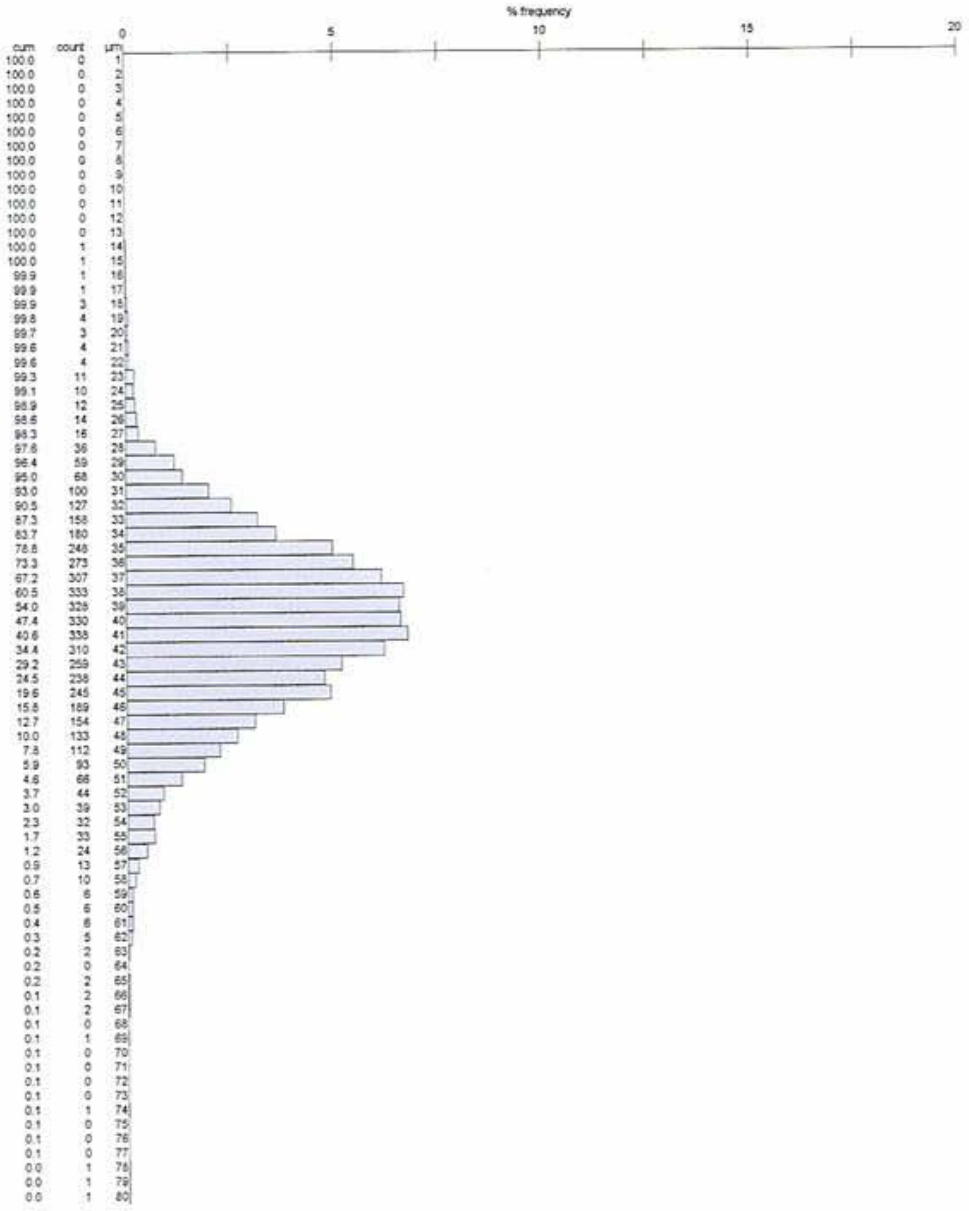
Operator:	Paul						
Client:	TEAM Research Group						
File:	S191379.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 23.5 µm	*SD:*	5.0 µm	*CV:*	21.3%	*Spin Fineness:*	22.9 µm
Curvature	*Mean:* 75.0 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	60.5%		
CF:	91.8%	**Duration (s):**	282				
Description:	H. Neal, Woolmark Top						



Appendix 6 - DEFRA Fibre Diameter Results

AWTA Laserscan

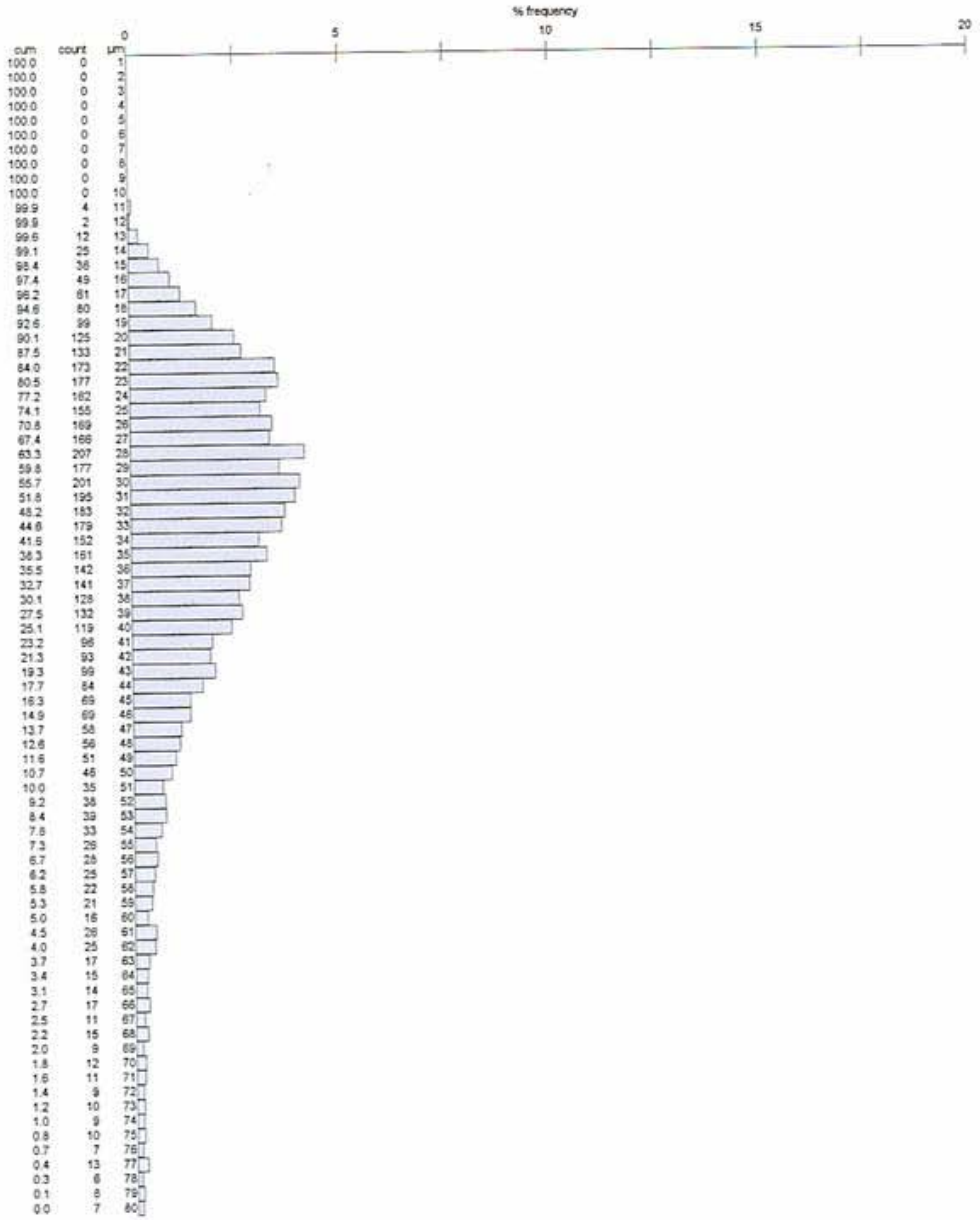
Operator:	Paul						
Client:	TEAM Research Group						
File:	S191374.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 40.4 µm	*SD:*	6.5 µm	*CV:*	16.1%	*Spin Fineness:*	37.8 µm
Curvature	*Mean:* 70.2 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	61.0%		
CF:	5.0%	**Duration (s):**	529				
Description:	H. Neal, DEFRA scaored top						



Appendix 7 - Dark Grey Herdwick Fibre Diameter Results

AWTA Laserscan

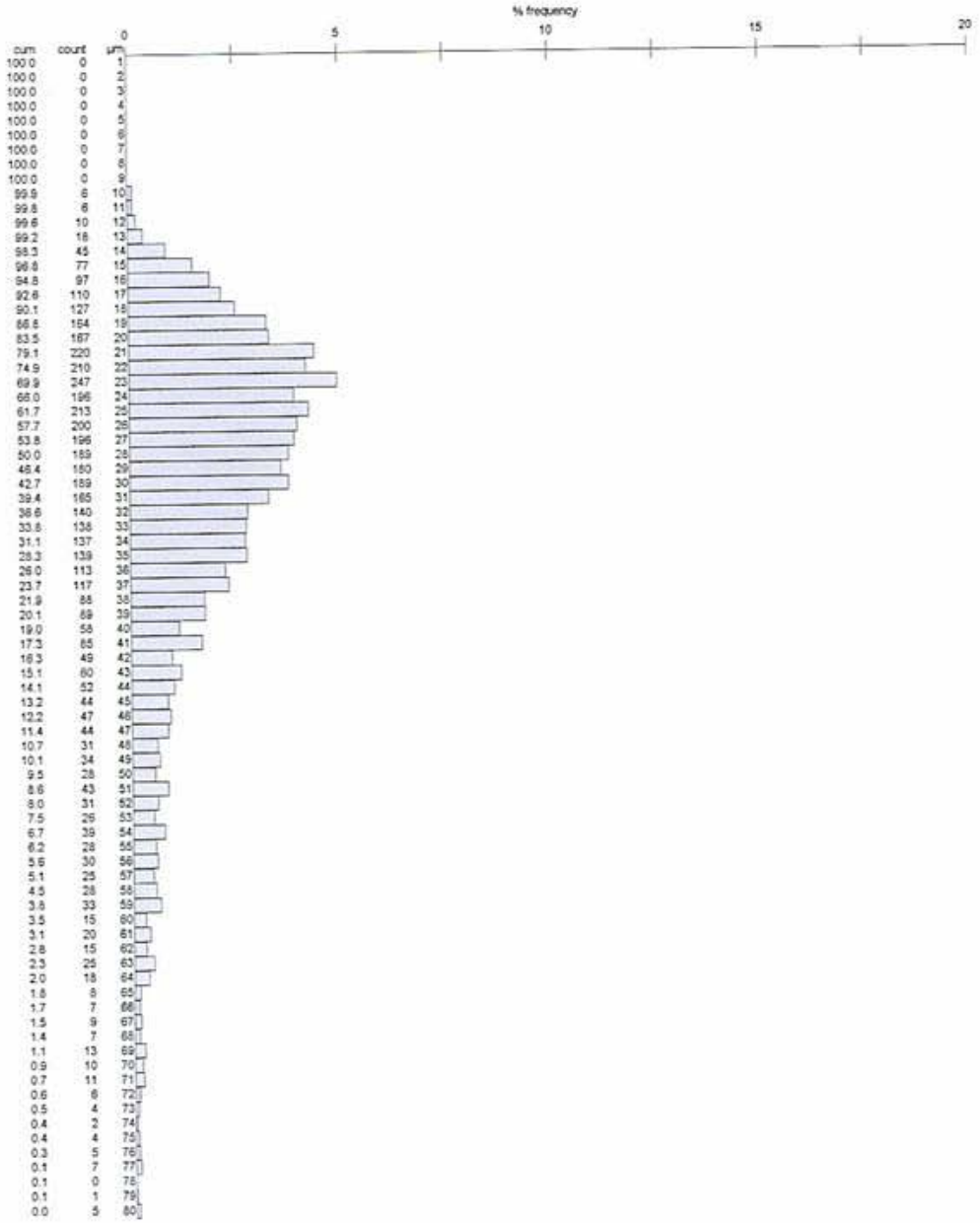
Operator:	Paul						
Client:	TEAM Research Group						
File:	S191375.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 34.3 µm	*SD:*	12.6 µm	*CV:*	36.8%	*Spin Fineness:*	39.2 µm
Curvature	*Mean:* 74.1 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	51.0%		
CF:	44.3%	**Duration (s):**	1038				
Description:	H. Neal, Scoured dark grey Hardwick, T. Chadwick						



Appendix 8 - Swaledale Fibre Diameter Results

AWTA Laserscan

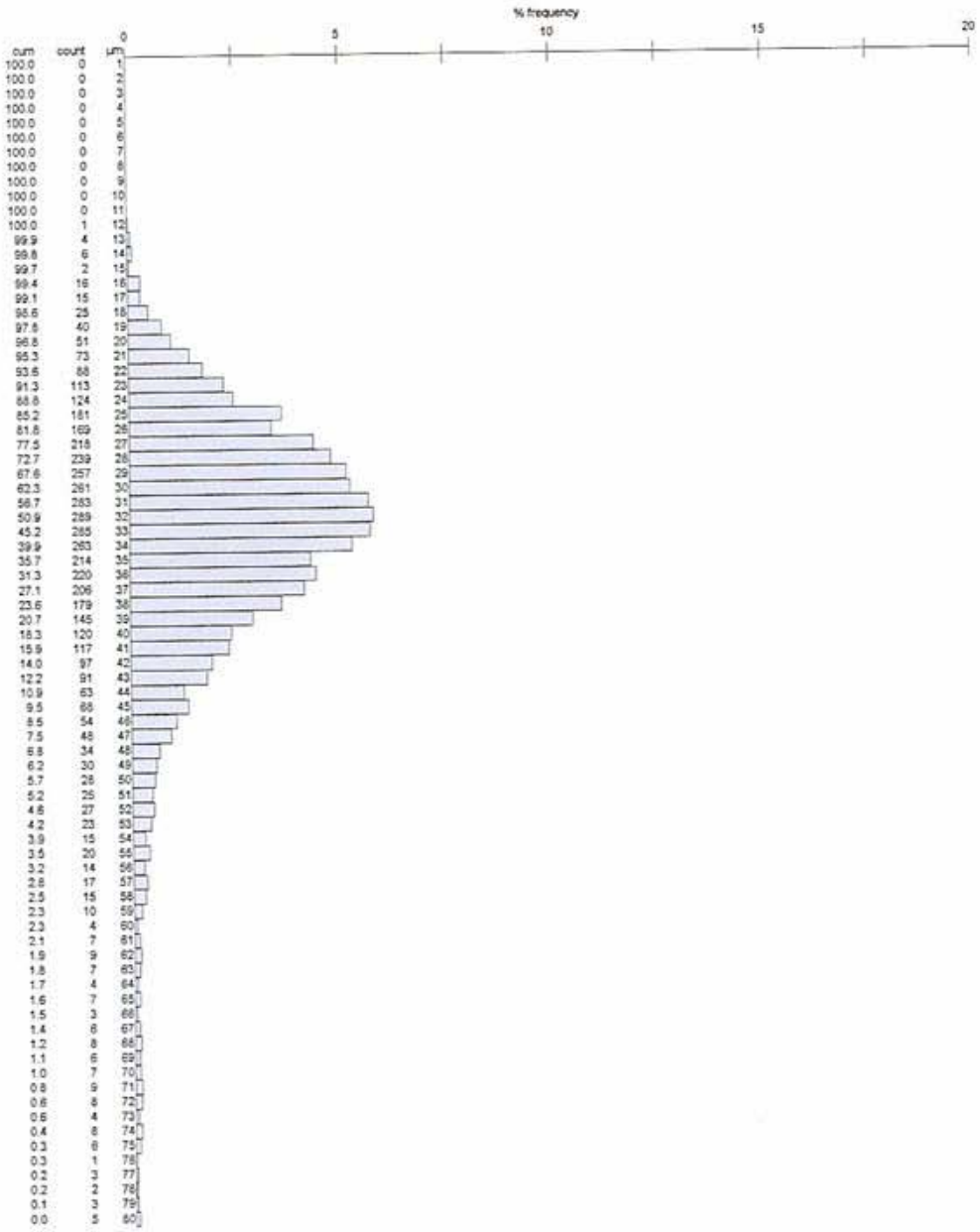
Operator:	Paul						
Client:	TEAM Research Group						
File:	S191378.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 31.3 µm	*SD:*	12.4 µm	*CV:*	39.5%	*Spin Fineness:*	36.9 µm
Curvature	*Mean:* 81.2 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	49.4%		
CF:	57.3%	**Duration (s):**	492				
Description:	H. Neal, Swaledale, T. Chadwick						



Appendix 9 - Crossbred Fibre Diameter Results

AWTA Laserscan

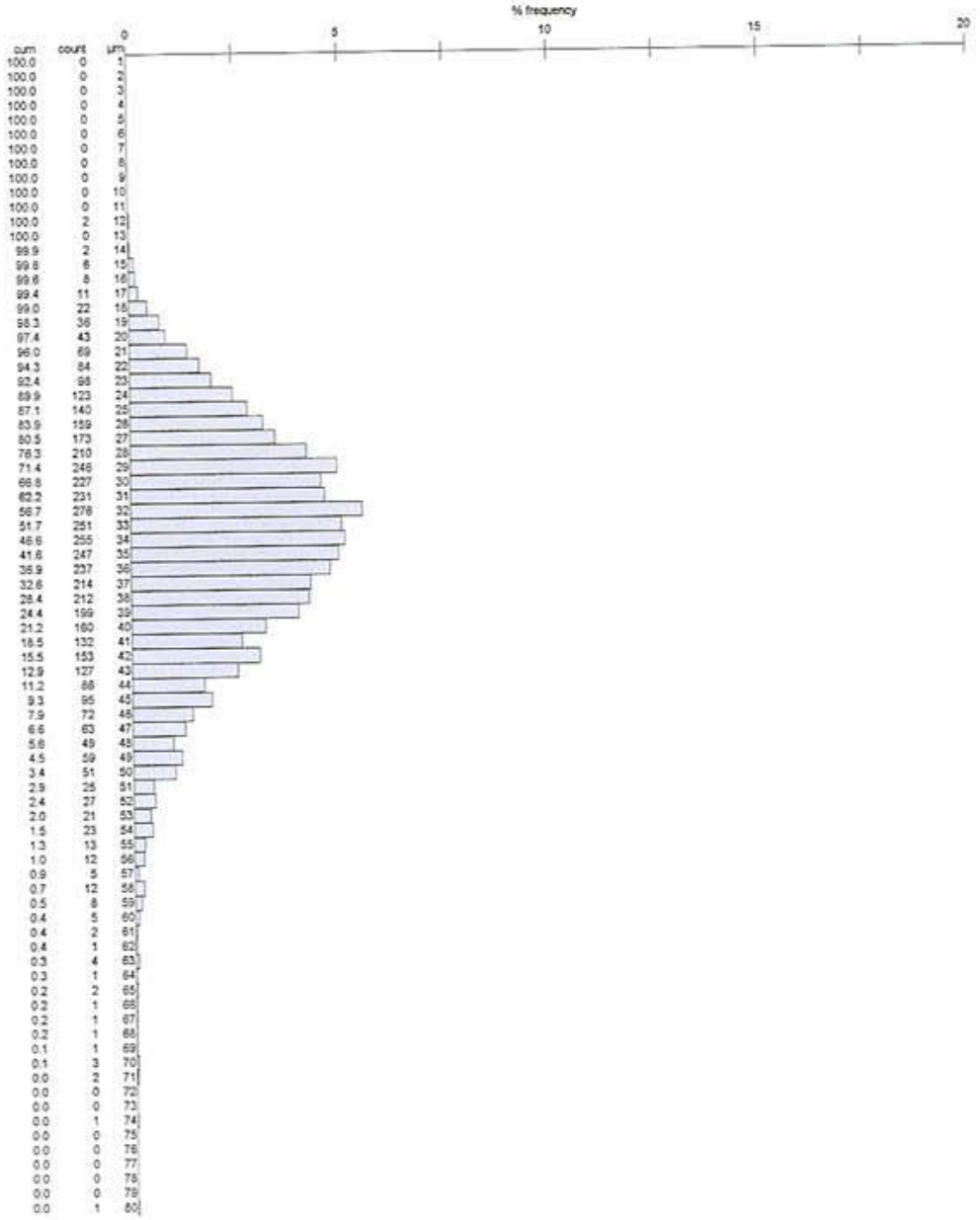
Operator:	Paul						
Client:	TEAM Research Group						
File:	S191376.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 34.1 µm	*SD:*	9.5 µm	*CV:*	27.9%	*Spin Fineness:*	35.4 µm
Curvature	*Mean:* 70.3 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	58.6%		
CF:	37.7%	**Duration (s):**	544				
Description:	H. Neal, Scoured crosses, T. Chadwick						



Appendix 10 - Halfbreds Fibre Diameter Results

AWTA Laserscan

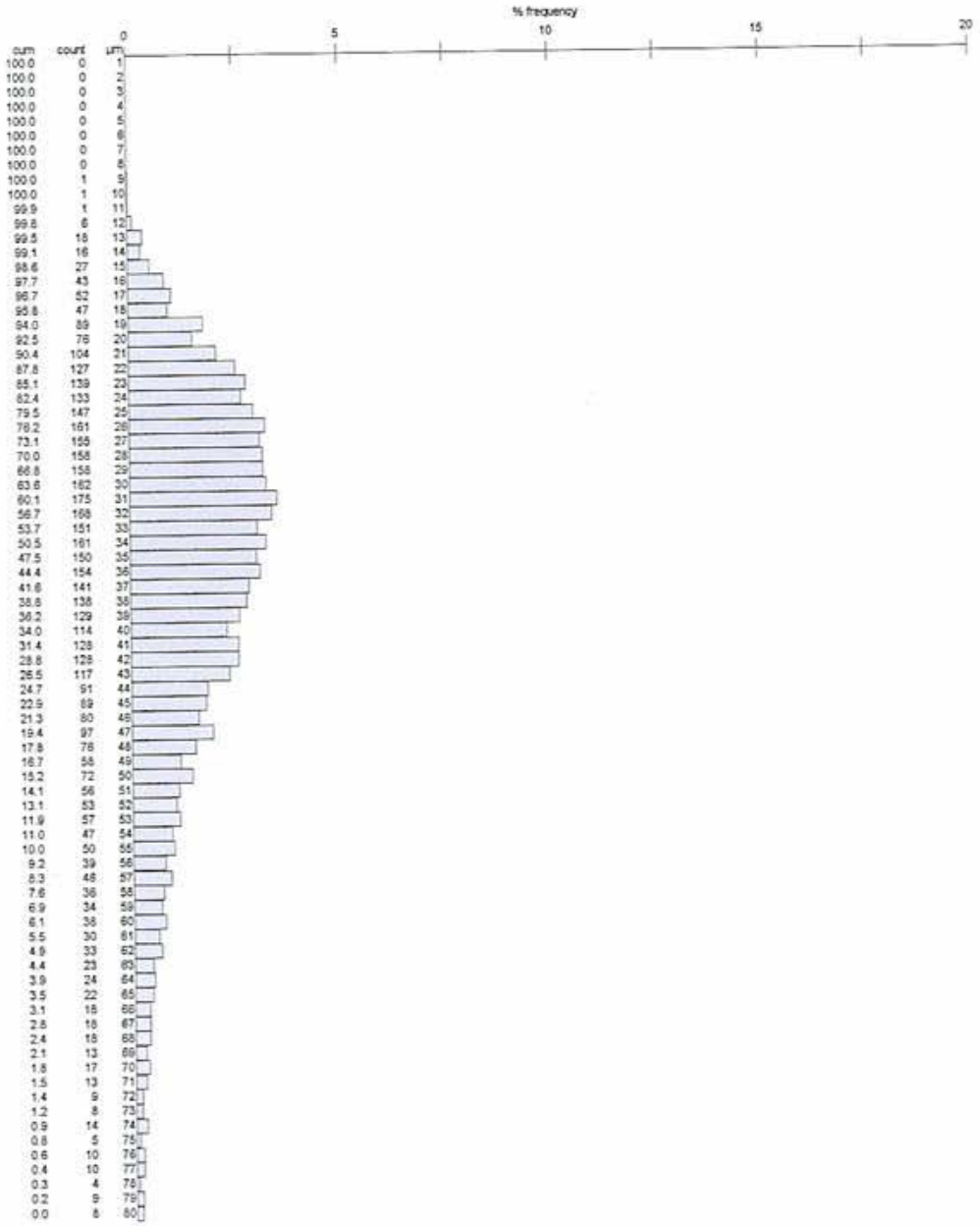
Operator:	Paul						
Client:	TEAM Research Group						
File:	S191373.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 34.5 µm	*SD:*	8.2 µm	*CV:*	23.8%	*Spin Fineness:*	34.4 µm
Curvature	*Mean:* 86.2 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	57.8%		
CF:	33.2%	**Duration (s):**	482				
Description:	H. Neal, Scoured Halfbreds, T. Chadwick						



Appendix 11 - Blackface Fibre Diameter Results

AWTA Laserscan

Operator:	Paul						
Client:	TEAM Research Group						
File:	S191377.DAT						
Sampled:	15 Jul, 2005						
Diameter	*Mean:* 36.8 µm	*SD:*	13.2 µm	*CV:*	35.9%	*Spin Fineness:*	41.5 µm
Curvature	*Mean:* 66.0 deg/mm						
Calibration:	CAL0101S19	**Snippets Counted:**	5000	**Acceptance:**	54.5%		
CF:	36.4%	**Duration (s):**	764				
Description:	H. Neal, Scoured Blach-face, T. Chadwick						



Appendix 12 - Chemtura Effluent Standard Data

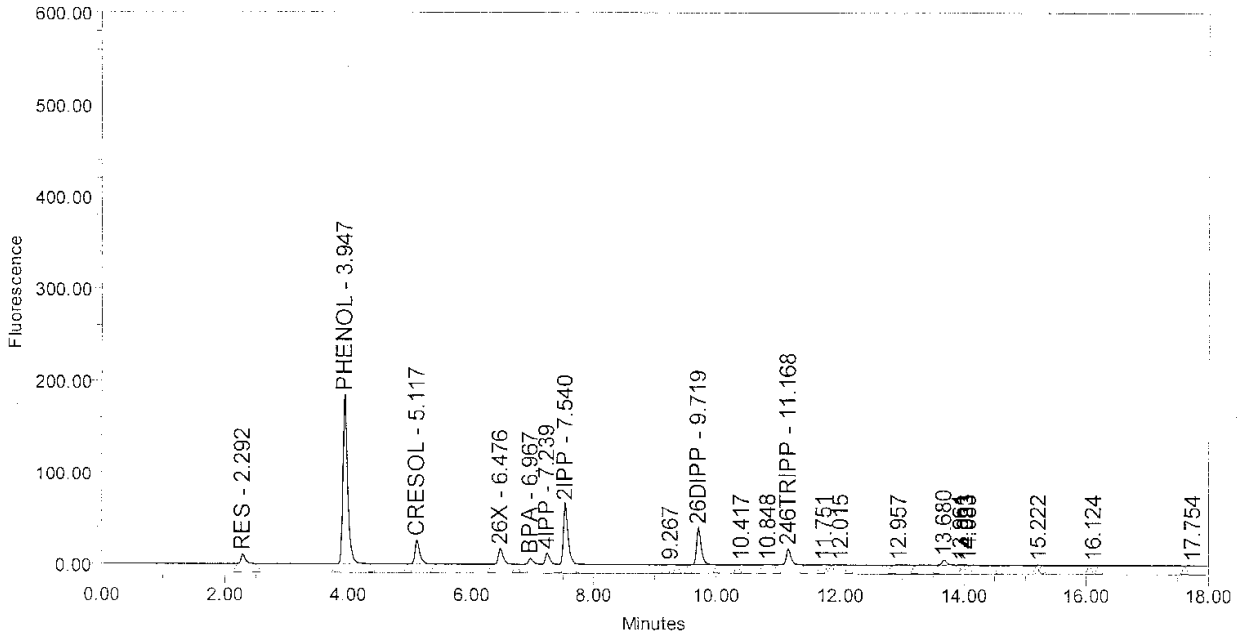
Individual Sample Report

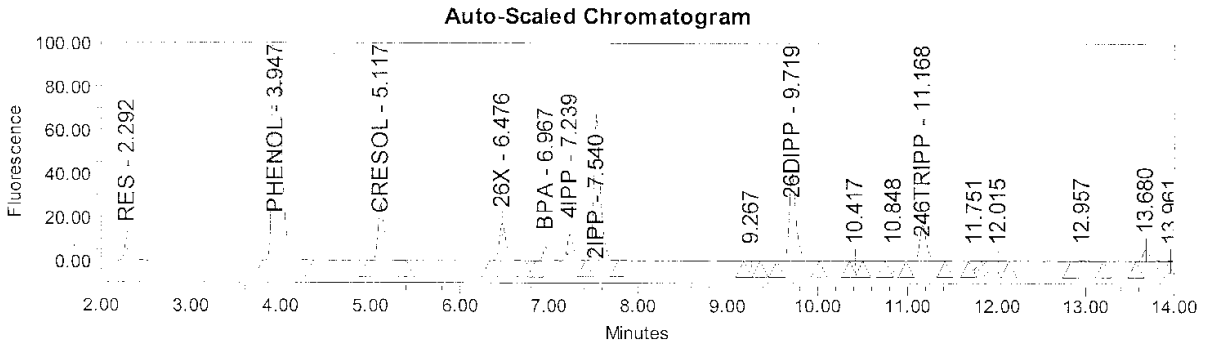
Reported by User: System

Project Name: ENVIRONMENTAL

SAMPLE INFORMATION

Sample Name:	EFFLUENT STD	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	7/9/2007 9:21:37 PM
Vial:	21	Acq. Method Set:	EFFLUENT
Injection #:	1	Date Processed:	7/9/2007 9:43:53 PM
Injection Volume:	10.00 ul	Processing Method:	EFFLUENT
Run Time:	22.0 Minutes	Channel Name:	474 Ch1
Sample Set Name:	EFFLUENT 090707	Proc. Chnl. Descr.:	





Individual Sample Report

Reported by User: System

Project Name: ENVIRONMENTAL

	Peak Name	RT	Area	Amount	Units
1	RES	2.292	48570	2.581	PPM
2	PHENOL	3.947	978025	16.164	PPM
3	CRESOL	5.117	135175	2.595	PPM
4	26X	6.476	92900	2.054	PPM
5	BPA	6.967	32162	2.159	PPM
6	4IPP	7.239	61952	2.133	PPM
7	2IPP	7.540	349245	6.142	PPM
8	26DIPP	9.719	209160	5.197	PPM
9	246TRIPP	11.168	88850	5.921	PPM
Sum				44.9	

Appendix 13 - Chemtura Effluent In Data

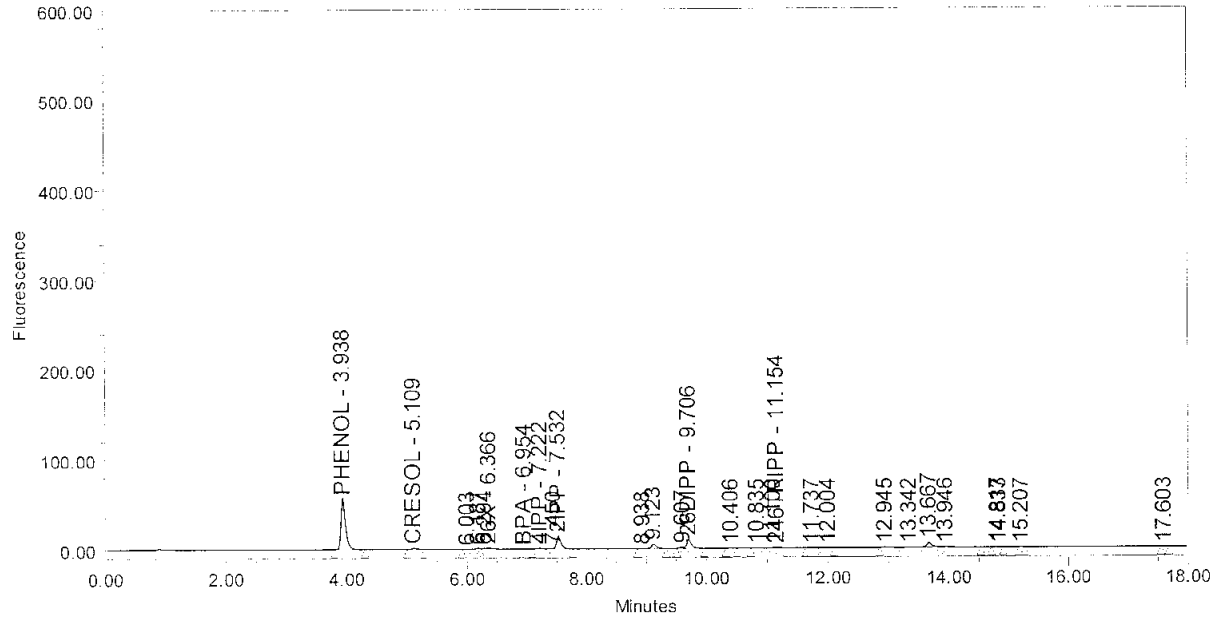
Individual Sample Report

Reported by User: System

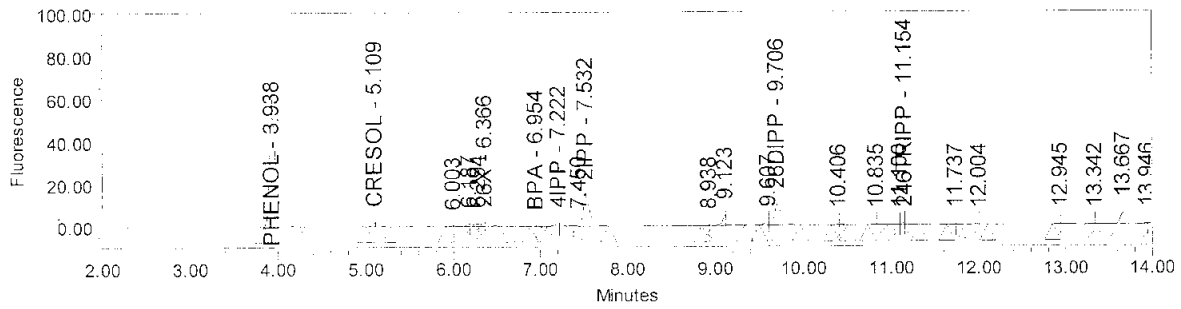
Project Name: ENVIRONMENTAL

SAMPLE INFORMATION

Sample Name:	IN	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	7/9/2007 10:31:05 PM
Vial:	23	Acq. Method Set:	EFFLUENT
Injection #:	1	Date Processed:	7/9/2007 10:53:22 PM
Injection Volume:	10.00 ul	Processing Method:	EFFLUENT
Run Time:	22.0 Minutes	Channel Name:	474 Ch1
Sample Set Name:	EFFLUENT 090707	Proc. Chnl. Descr.:	



Auto-Scaled Chromatogram



Individual Sample Report

Reported by User: System

Project Name: ENVIRONMENTAL

	Peak Name	RT	Area	Amount	Units
1	PHENOL	3.938	296240	9.803	PPM
2	CRESOL	5.109	8450	0.325	PPM
3	26X	6.366	10989	0.495	PPM
4	BPA	6.954	470	0.063	PPM
5	4IPP	7.222	6797	0.466	PPM
6	2IPP	7.532	74406	2.622	PPM
7	26DIPP	9.706	51733	2.649	PPM
8	246TRIPP	11.154	5069	0.703	PPM
Sum				17.1	

Appendix 14 - Chemtura Effluent Out Data

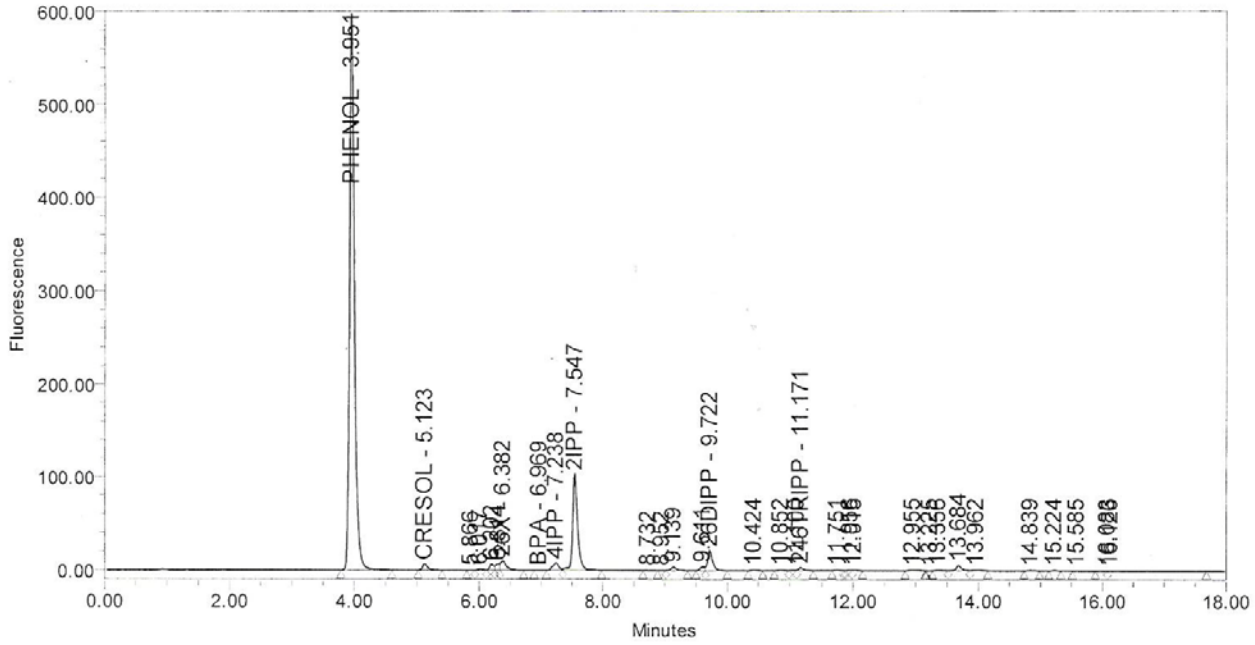
Individual Sample Report

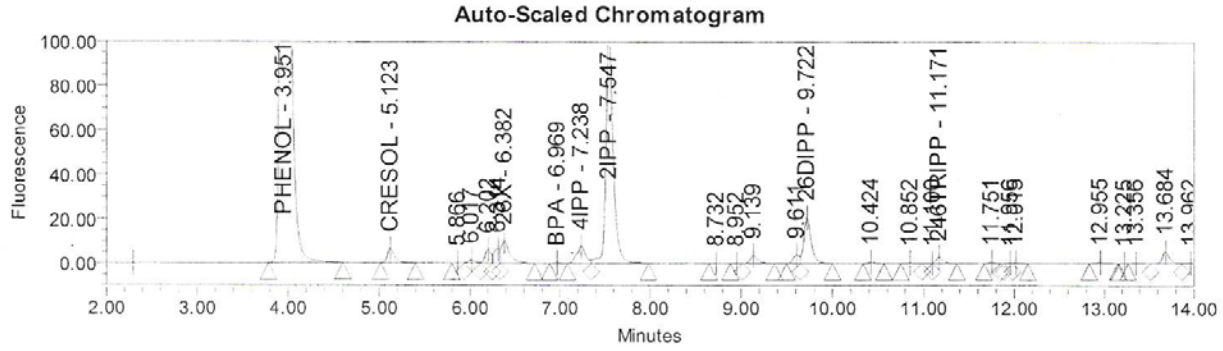
Reported by User: System

Project Name: ENVIRONMENTAL

SAMPLE INFORMATION

Sample Name:	OUT	Acquired By:	System
Sample Type:	Unknow n	Date Acquired:	7/9/2007 10:07:54 PM
Vial:	22	Acq. Method Set:	EFFLUENT
Injection #:	1	Date Processed:	7/9/2007 10:30:10 PM
Injection Volume:	10.00 ul	Processing Method:	EFFLUENT
Run Time:	22.0 Minutes	Channel Name:	474 Ch1
Sample Set Name:	EFFLUENT 090707	Proc. Chnl. Descr.:	





Individual Sample Report

Reported by User: System

Project Name: ENVIRONMENTAL

	Peak Name	RT	Area	Amount	Units
1	PHENOL	3.951	3268600	108.165	PPM
2	CRESOL	5.123	34530	1.326	PPM
3	26X	6.382	65256	2.937	PPM
4	BPA	6.969	820	0.110	PPM
5	4IPP	7.238	52206	3.581	PPM
6	2IPP	7.547	575008	20.263	PPM
7	26DIPP	9.722	113069	5.790	PPM
8	246TRIPP	11.171	14773	2.049	PPM
Sum				144.2	

Appendix 15 - A H Marks Treated Effluent Data

A H MARKS 07008342

TE150 **Final effluent 301H1**

1693

Component	Result	Units	Lower	Upper	Sentence
pH	6.5				
Density	1.073	g/ml			
COD	17600	mg/l			
PHENOL	3	mg/l			
O-CRESOL	13	mg/l			
2-CP	5	mg/l			
4-CP	2	mg/l			
2,6-DCP	2	mg/l			
2,4-D	1	mg/l			
MCPA	6	mg/l			
6-COC	0	mg/l			
PCOC	64	mg/l			
2,4-DCP	98	mg/l			
2,4-DP	4	mg/l			
CMPP	18	mg/l			
2,4-DB	1	mg/l			
MCPB	0	mg/l			
2,4,6-TCP	2	mg/l			
TOTAL PHENOLS	189	mg/l			
TOTAL PHENOXIES	30	mg/l			
Butyl BIT	0	mg/l			

Sample Type:	Environmental	Received Date:	23-Jul-07
Product Group:	Treated effluent	Received Time:	00:20
Business Group:	Env	Completion Date:	23-Jul-07
Submitter:	Plant 42	Completion Time:	03:25
Submitter EMail:	Plant42 QCResults/Wy	Turn Round Time:	3 Hrs 5 Mins
Storage Period:	Yrs	Target Turn Round Time:	4 Hrs

A H MARKS

07008342

TE150 **Final effluent 301H1**

1693

Component	Result	Units	Lower	Upper	Sentence
Iso-Butanol	0.0	mg/l			
IPA	148.9	mg/l			
n-Butanol	28.1	mg/l			
Toluene	2.6	mg/l			
Ethyl Benzene	0.5	mg/l			
M-Xylene/P-Xylene	1.4	mg/l			
O-Xylene	0.7	mg/l			
Total Xylenes	2.6	mg/l			
2EH	615.7	mg/l			
Total Nitro	1.7	mg/l			
Glycolic Acid	7968	mg/l			
Lactic Acid	10717	mg/l			
ACPA	954	mg/l			

2EH = 2 ethyl-hexanol

Sample Type:	Environmental	Received Date:	23-Jul-07
Product Group:	Treated effluent	Received Time:	00:20
Business Group:	Env	Completion Date:	23-Jul-07
Submitter:	Plant 42	Completion Time:	03:25
Submitter EMail:	Plant42 QCResults/Wy	Turn Round Time:	3 Hrs 5 Mins
Storage Period:	Yrs	Target Turn Round Time:	4 Hrs

23 July 2007